https://doi.org/10.18778/8331-401-3.03

Chapter 2

Footwear Innovation to Improve the Comfort of Use

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2.1. Definition of the Comfort of Footwear Users and Improvement Prospects

Footwear satisfies diverse and constantly changing human needs, and it may significantly shape the development and efficiency of the foot in both positive and negative terms. According to orthopaedic doctors, non-physiological footwear becomes the cause of many diseases and deformities of the feet, which are often irreversible. Footwear should provide for certain functions:

- Protective;
- Hygiene and comfort;
- Social and aesthetic.

The protective function is the basic function that footwear must fulfil:

- protection of the foot against mechanical factors (mechanical injuries, pressure), unevenness of the ground;
- protection of the foot against climatic factors (temperature, precipitation);
- protection against liquid agents (water, acids, alkalis, fats, salt solutions);
- protection against radiation, variability of electromagnetic fields, electrostatic impact, which are harmful to human health.

Hygiene and comfort are the properties of footwear that ensure the well-being of the wearer and the healthy condition of the foot. Footwear should also allow the feet to develop and function naturally:

- Maintenance of an optimum microclimate at foot level through ventilation and oxidation of the foot skin, permeation of water vapour from the inside to the outside, absorption and desorption of liquids and vapour, mechanical vapour transmission, internal heat dissipation;
- Antimicrobial protection;
- Providing biomechanical support and movement through internal volume and dimensions corresponding to correct static and dynamic dimensions, ensuring preservation of natural posture, anti-slip and shock absorption;
- Maintaining the health of the body through correct and anatomical design;
- Influencing the reflex points of the presopuncture.

It would be good if the footwear also fulfilled social and aesthetic functions:

- Compatibility with the current fashion;
- Retention of original aesthetic appearance as long as possible throughout the use of footwear;
- Price.

Nowadays, with the changing environment and conditions of human life, technological advancement, and especially with widespread manufacture chemicalisation, the problem of comfort and safety in the use of products, including footwear for general use, is most relevant.

The comfort of footwear use is a subjective feeling of each user and is therefore difficult to define and evaluate. The comfort of use is also called physiological comfort because it should primarily satisfy the physiological needs of the foot.[1]

Comfortable footwear should ensure the well-being of the wearer, the healthy condition of the feet and allow the feet to develop naturally and function in accordance with their physiology and working functions. Comfort is the function that applies to all types of footwear (casual, safety, work, sports). Aspects of comfort relate to the appropriate shape, size of the footwear, as well as the properties of the raw material in combination with the anthropometric characteristics that are individual for each user.[2]

Comfortable footwear is important from the point of view of psychology and overall health, as it prevents foot deformation, corns, calluses and even varicose veins. As footwear comfort is a subjective perception of the user, there are few reports on its global improvement in the related literature. The overall wearer

1 I. Duda, (2005), *Comfort and safety issues in footwear,* "Scientific Journals of the Cracow University of Economics", vol. 685, Kraków, pp. 5–18.

2 W. Serweta, J. Wójcik, M. Matusiak, K. Ławińska, B. Szałek, (2020), *Research on the Possibilities of Polymer Textile Applications as Footwear Packages to Improve Health Properties.* "Fibres & Textiles in Eastern Europe", vol. 4, no. 142, Łódź, pp. 89–94.

comfort rating scale is, among others, assessed by the Kruskal-Wallis test. In this test, patients rate shoe comfort features by means of nine categories (overall shoe comfort, heel cushioning, side-to-side support, arch height, heel fit, ball of the foot width, heel width, ball of the foot cushioning, length).[3]

In the related literature, optimal thermal conditions, an optimal microclimate inside the footwear, which is related to the selection of suitable materials (high quality, moisture absorption and wicking) constitute frequently mentioned categories of comfort improvement. A study published in the International Journal of Fashion Design assessed the footwear preferences and microclimates of footwear made of leather and mesh spacer fabric. Subjective feelings when wearing both types of footwear were investigated. Out of the 80 respondents, the majority preferred sports shoes made of mesh fabric, as leather sports shoes retained more heat and moisture on the feet. The perception of temperature, moisture, and overall comfort of the footwear is influenced by the test subjects' criteria such as gender, age, and the type of activity.[4]

The materials used for manufacturing both the shoe upper and lining as well as the innersole have the greatest impact upon the footwear thermal comfort. Diverse arrangements of materials were tested for absorption and permeability, which was closely related to the footwear comfort.[5] The authors, based on literature sources,[6, 7] assumed that the humidity inside the footwear in the range of 70–85% is partial discomfort, and above 85% it is full comfort. They defined the generalised discomfort index DI = TRH>70% • DIRH>70%, where DI was the generalised discomfort index, TRH>70% was the time during exercise when the relative humidity was higher than 70%, and DIRH>70% was the discomfort index for relative humidity higher than 70%. They carried out a statistical analysis that allowed to distinguish materials used for the shoe uppers and lining, that may minimise the perceived discomfort associated with humidity inside the footwear. They tested a variety of materials and their different combinations (Table 2.1., 2.2. and 2.3.).

3 B. Hurst, H. Branthwaite, A. Greenhalgh et al., (2017), *Medical-grade footwear: the impact of fit and comfort,* "Journal of Foot and Ankle Research", vol. 10, no. 2.

4 K. Yick, A. Yu, P. Li, (2019), *Insights into footwear preferences and insole design to improve thermal environment of footwear*, "International Journal of Fashion Design, Technology and Education", vol. 12, no. 3, pp. 325–334.

5 W. Serweta, Z. Olejniczak, M. Matusiak, (2019), *Improve of Footwear Comfort Sensation with Material Packages and Knitted Fabrics*, "FIBRES & TEXTILES in Eastern Europe", vol. 27, no. 3(135), Łódź, pp. 85–90.

6 F. Langmaier, M. Mladek, (1973), *Studie mikroklimatu obuvi*, „Kozarstvi", vol. 4, pp. 96–101.

7 F. Langmaier, (1990), *Hygiena a komfort obutenohy*, „Kozarstvi", vol. 12, pp. 345–349.

Table 2.1. Types of lining fabrics used in the study

Type of lining fabrics	Symbol	Water vapour permeability [mg/cm² h]	Water vapour coefficient, [mg/cm²]
3D knitted fabric with PA fibre	MP1	30.5 ± 4.2	245.0 ± 17.5
3D knitted 'a-jours' fabric with PA	MP2	45.8 ± 0.9	367.4 ± 6.1
Trevira	MP8	21.5 ± 1.7	173.3 ± 11.5
Knitted fabric PE (small loop)	MP39	37.7 ± 2.2	301.3 ± 3.2
Microfibre PE	MP41	21.3 ± 3.2	170.7 ± 7.1
Knitted fabric PE (bigger loop)	MP42	42.6 ± 5.2	341.7 ± 8.2

Source: W. Serweta, Z. Olejniczak, M. Matusiak, (2019), *Improve of Footwear Comfort Sensation with Material Packages and Knitted Fabrics*, "FIBRES & TEXTILES in Eastern Europe", vol.27, no. 3(135), Łódź, pp. 85–90.

Table 2.2. Types of leather lining used in the study

Type of leather lining	Symbol	Water vapour permeability [mg/cm² h]	Water vapour coefficient, [mg/cm²]
Cow split grinded leather	SP1	15.8 ± 0.8	136.0 ± 4.5
Cow leather	SP2	13.6 ± 1.1	128.3 ± 8.2
Pig grain leather	SP3	15.3 ± 0.6	113.6 ± 1.8

Source: W. Serweta, Z. Olejniczak, M. Matusiak, (2019), *Improve of Footwear Comfort Sensation with Material Packages and Knitted Fabrics*, "FIBRES & TEXTILES in Eastern Europe", vol. 27, no. 3(135), Łódź, pp. 85–90.

Table 2.3. The set of materials analysed

Group I (materials compiled with MP41)	Group II (materials compiled with MP39)	Group III (leather lining)
MP8 + MP41	MP8 + MP39	SP1
MP42 + MP41	MP42 + MP39	SP2
MP2 + MP41	MP2 + MP39	SP3
MP1 + MP41	MP1 + MP39	

Source: W. Serweta, Z. Olejniczak, M. Matusiak, (2019), *Improve of Footwear Comfort Sensation with Material Packages and Knitted Fabrics*, "FIBRES & TEXTILES in Eastern Europe", vol.27, no. 3(135), Łódź, pp. 85–90.

The best materials are given as follows: MP2 – MP41 – SW1 and MP2 – MP39 – SW1 (given above) and for components corresponding with the SW4 upper: MP2 – MP41 – SW4 (DI = 0.09) and MP2 – MP39 – SW4 (DI fluctuating around 0.10). It is worth noting that only the MP41 and MP39 materials were selected because for the other materials, that had accounted for changes in the discomfort indexes recorded after a longer time of use, namely 30-minute exertion, the changes were insignificant.

According to the minimised discomfort index, the best materials out of those tested were: SP1 (DI = 0.24), SP2 (DI = 0.36) and SP3 (DI = 0.29). SP1 regarded as the best leather lining.

The analysis of the relationship between combinations of the lining and upper materials and discomfort index values obtained on the basis of exertion simulation confirmed that differences existed and were statistically significant. The optimal choice of footwear materials may substantially minimise the footwear discomfort. It is a very important factor.

The effect of comfort on running economy and injury risk was also assessed in relation to oxygen consumption (economic perspective) and biomechanical parameters (injury perspective) during walking and running. However, this study found that an increase in comfort did not lead to a reduction in oxygen consumption and significant changes in biomechanical parameters.[8]

The primary footwear components of interest to improve performance include midsole material, weight, longitudinal bending stiffness,[9] shock absorption.[10]

Technically, shoe comfort may be defined by means of the conjugation of several factors, namely, fitting, in-shoe thermal and humidity, plantar pressure distribution and ground impact forces. Among those parameters, ground impact force is one of the most significant aspects to take into consideration in the development of comfortable shoes since it contributes to discomfort but may also induce injuries and in some cases pain.[11]

However, the definition of shock absorption is not completely consensual and the range of its acceptable values is not clear. Shock absorption properties are related to the capability of cushioning the impact of ground forces that affect human locomotion. When walking, human gait involves repeated loading (nearly 60% of

8 J. Jindorfer, J. Kröll, H. Schwameder, (2020), *Does enhanced footwear comfort affect oxygen consumption and running biomechanics?*, "European Journal of Sport Science", vol. 20, no. 4, pp. 468–476.

9 E. Day, M. Hahn, (2020), *Optimal footwear longitudinal bending stiffness to improve running economy is speed dependent*, "Footwear Science", vol. 12, no. 1, pp. 3–13.

10 R.M. Silva, J.L. Rodrigues, V.V. Pinto, M.J. Ferreira, R. Russo, C.M. Pereira, (2009), *Evaluation of shock absorption properties of rubber materials regarding footwear applications*, "Polymer Testing", vol. 28, no. 6, pp. 642–647.

11 M.W. Whittle, (1999), *Generation and attenuation of transient impulsive forces beneath the foot: a review*, "Gait Posture", vol. 10, no. 3, p. 264–275.

one's body weight is loaded abruptly, in less than 20 ms, onto the ipsilateral limb) each time the foot hits the ground in the early stance phase of the gait cycle.[12] This results in a transient force transmitted up to the skeleton, as a shock wave that runs through the human body from feet toward the upper extremities. Impact ground forces present values that may reach up to 120 and 250 percent of the person's body weight in walking and running conditions, respectively.[13] Impact loads generated during gait have been implicated in several injuries and health problems, such as stress fractures, Type 1 shin splints, cartilage breakdown, osteoarthritis, knee injuries and low back pain.[14] Proper cushioning will attenuate those impact forces and protect the musculoskeletal system from potential injury.

The heel-pad is the natural mechanism to attenuate the generated shock wave. Several studies[15, 16, 17] have been conducted in order to understand the mechanical properties of the heel pad linked to the impact force attenuation during locomotion, however the published results are still under some controversy.[18] Moreover, the common use of footwear since birth has decreased the attenuating capability of the heel-pad mechanism in absorbing the impact of ground forces.[19]

The foot-ground interface depends both on the shoe and floor material and their interaction, therefore those interfaces play an important role in providing suitable biomechanical characteristics, injury prevention and reducing discomfort.

Cellular materials (e.g. foams, ethyl-vinyl-acetate, polyurethane, etc.) are commonly accepted as materials that prove good cushioning properties, however those soft materials show lower tear strength, higher abrasion and tend to deform gradually, leading to an uncomfortable situation, and in some cases may contribute significantly to back pain, musculoskeletal disorders and injuries. Nevertheless, in

12 R. Bogey, *Gait analysis*, updated 23.02.2023, Gait Analysis: Fundamentals, Methods of Analysis, Normal Gait (medscape.com).

13 B.M. Nigg, D. Stefanyshyn, G. Cole, P. Stergiou, J. Miller, (2003), *The effect of material characteristics of shoe soles on muscle activation and energy aspects during running*, "Journal of Biomechanics", vol. 36, no. 4, p. 569.

14 R.S. Goonetilleke, (1999), *Footwear cushioning: relating objective and subjective measurements*, "Human Factors", vol. 41, no. 2, pp. 241–256.

15 P. Aerts, R.F. Ker, D. De Clercq, D.W. Ilsley, R.M. Alexander, (1995), *The mechanical properties of the human heel pad: a paradox resolved*, "Journal of Biomechanics", vol. 28, no. 11, pp. 1299–1308.

16 A. Gefen, M. Megido-Ravid, Y. Itzchak, (2001), *In vivo biomechanical behavior of the human heel pad during the stance phase of gait*, "Journal of Biomechanics ", vol. 34, no. 12, pp. 1661–1665.

17 K-J. Chi, D. Schmitt, (2005), *Mechanical energy and effective foot mass during impact loading of walking and running*, "Journal of Biomechanics", vol. 38, no. 7, pp. 1387–1395.

18 R.E. Weijers, A.G. Kessels, G.J. Kemerink, (2005), *The damping properties of the venous plexus of the heel region of the foot during simulated heelstrike*, "Journal of Biomechanics", vol. 38, no. 12, pp. 2423–2430.

19 U. Jorgensen, F. Bojsenmoller, (1986), *Joint forces in extension of the knee: Analysis of a mechanical model*, "Acta Orthopaedica Scandinavica", vol. 57, no. 1, pp. 41–46.

order for a good shock absorption behaviour in footwear, a compromise between the shock absorption properties of a material and its elasticity and resistance to fatigue has to be reached. For this reason, rubber materials are still preferred for outsole manufacture, due to their particular physical properties such as high tear and tensile strength, lower abrasion, resistance to oils and durability.[20]

Methodologies for evaluation of a material's shock absorption properties are limited in number, and none of them is completely accepted by all of the economic operators in the footwear market. Standardised methodologies can be found in the procedure A of ASTM F1614-06 (dynamic analysis)[21] and EN ISO 20344:2004-5.14 (static analysis).[22] The former one evaluates the impact response properties of athletic shoes using an impact test and the latter one is a test method for safety footwear, that evaluates the energy absorption of the seat region.

Other methodologies use a similar approach to assess the shock absorption properties of the contact surfaces. For example, the European standard EN 14808:2005[23] (based on the Berlin Artificial Athlete) defines a method of determining the shock absorption characteristics of sports surfaces by means applying a 20 kg weight that falls onto a spring placed on the tested item. In the European standard EN 1177:2008[24] and equivalent ASTM 1292:2004[25] the test methods of determining the critical fall height are defined, based on impact attenuation of surfacing playground materials.

There are also other non-standardised methodologies such as the SATRA PM 142 Shock Absorption Test Method,[26] and the IBV shock absorption testing methodology.[27] The SATRA PM 142 differs from the standardised procedure A of ASTM F1614-06 to the extent of small details in terms of the fixed anvil assembly. As far as the first method is concerned, the fixed anvil consists of a single block weighing 8.5 kg while in the case of the second one the total 8.5 kg mass includes a 200 g detachable tup. Another important difference is the geometry of the tup: the SATRA PM 142 test method uses a spherical tup while the ASTM F1614-06 test makes use of a flat tup with rounded edges. The IBV test method is a completely different approach in which a drop test machine is used for simulating the effect

20 R.M. Silva, J.L. Rodrigues, V.V. Pinto, M.J. Ferreira, R. Russo, C.M. Pereira, (2009), *Evaluation…*

21 ASTM F1614-06, *Shock Attenuation Properties of Materials Systems for Athletic Footwear*, American Society for Testing and Materials, 2006.

22 EN ISO 20344, *Personal Protective Equipment – Test Methods for Footwear* (2004).

23 EN 14808, *Surfaces for Sports Areas – Determination of Shock Absorption* (2005).

24 EN 1177*, Impact Attenuating Playground Surfacing – Determination of Critical Fall Height* (2008).

25 ASTM F1292-04, *Standard Specification for Impact Attenuation of Surfacing Materials within the Use Zone of Playground Equipment* (2004).

26 S. Tailby, (2003), *Falling mass shock absorption test "SATRA Bulletin*", October, p. 17.

27 J.V. Durá, A.C. García, J. Solaz, (2002), *Testing shock absorbing materials: the application of viscoelastic linear model*, "Sports Engineering", vol. 5, no. 1, pp. 9–14.

of the first stage of walking on materials. This method is intended to evaluate the dynamic stiffness and dissipated energy ratio.

Verdejo and Mills[28] also proposed an impact machine to analyse the changes in the mechanical response of shoe midsole foams. In their work they analysed the changes in stress-strain responses of foams under repeated impacts that simulated heel strikes. The key design parameters of the impact machine identified included the impact frequency and the peak pressure. A different approach was made by Goonetilleke and Ravinda, these authors used a 20-participant panel to evaluate the perceived levels of cushioning (PLC), which in turn was correlated with the footwear impact test results. They reported that, during walking, the magnitude of the peak deceleration on the impact tester appeared to be a good prediction of the PLC. Moreover, they concluded that impact characterisations could reveal important differences between materials and how they were perceived during activity.[29]

2.2. Antimicrobial Protection

Antimicrobial protection is one of the hygiene and comfort functions that footwear should fulfil. Bacterial and/or fungal colonisation of footwear causes detrimental effects such as user discomfort, reduced mechanical resistance of footwear materials (e.g. leather, textiles) or persistent odour from isovaleric acid that takes its origin when Staphylococcus epidermidis, the resident species of the normal bacterial flora of the skin, breaks down leucine present in sweat.[30] Therefore, functional materials with antimicrobial properties may prolong the economic life of footwear, thereby reducing costs and improving overall user comfort.[31]

A way to eliminate or inhibit the growth of microorganisms on footwear materials is, in addition to foot care and hygiene, the use of antimicrobial agents.[32] Chemical antimicrobial agents such as silver, copper oxides, zinc oxides, quaternary ammonium

28 R. Verdejo, N.J. Mills, (2004), *Simulating the effects of long distance running on shoe midsole foam*, "Polymer Testing", vol. 23 no. 4, pp. 567–574.

29 R.S. Goonetilleke, (1999), *Footwear cushioning…*

30 M.M. Sánchez-Navarro, M.Á. Pérez-Limiñana, F. Arán-Ais, C. Orgilés-Barceló, (2015), *Scent properties by natural fragrance microencapsulation for footwear applications*, "Polymer International", vol. 64, no. 10, pp. 1458–1464.

31 K. Ara, M. Hama, S. Akiba, K. Koike, K. Okisaka, T. Hagura, T. Kamiya, F. Tomita, (2006), *Foot Odour Due to Microbial Metabolism and its Control*, "Canadian Journal of Microbiology", vol. 52, no. 4, pp. 357–364.

32 M.M. Sánchez-Navarro, M.Á. Pérez-Limiñana, F. Arán-Ais, C. Orgilés-Barceló, (2015), *Scent properties…*

salts, borates, 3-iodo-2-propynyl butylcarbamate (IPBC), zinc pyrithione, etc., are used in the footwear industry. However, some of those are hazardous to the normal microflora of the foot skin and have irritant, harmful and toxic properties for the natural environment and human health. An alternative may arise from natural antimicrobial agents such as essential oils since their action against bacteria and fungi has been confirmed by numerous scientific studies.[33, 34, 35, 36, 37, 38, 39, 40]

Essential oils are extracted from plants such as cinnamon, mint, thyme, sage, clove, basil and rosemary. They are volatile substances, so when applied to materials, they have a short-lived effect, besides being chemically unstable and prone to oxidative degradation and loss of volatile compounds, especially when exposed to oxygen, light, moisture and temperature. Encapsulation of the essential oil eliminates those disadvantages with regard to the functionalisation of footwear materials, and furthermore provides controlled release properties expected by the footwear market.

Several scientific studies have shown that the encapsulation process increases the stability of essential oils by protecting them from external factors: oxygen, light radiation and reduces their volatility, giving materials a long-lasting effect. Microencapsulation plays an important role in obtaining smart textile and leather coatings.

33 Ibidem.

34 C. Chirilă, V. Deselnicu, M.D. Berechet, (2017), *Footwear Protection against Fungi Using Thyme Essential Oil*, "Leather and Footwear Journal", vol. 17, no. 3, pp. 173–178.

35 C. Chirilă, M. Crudu, V. Deselnicu, (2014), *Comparative Study regarding Resistance of Wet-White and Wet-Blue Leather to the Growth of Fungi*, "Leather and Footwear Journal", vol. 14, no. 2, pp. 107–120.

36 D.C. Deselnicu, A.M. Vasilescu, A.A. Purcarea, G. Militaru, (2014), *Sustainable Consumption and Production in the Footwear Sector*, "Leather and Footwear Journal", vol. 14, no. 3, pp. 159–180.

37 I.A. Radwan, A.H. Abed, M.R. Abeer, R.A. Ibrahim, A.S. Abdallah, (2014), *Effect of Thyme, Clove and Cinnamon Essential Oils on Candida albicans and Moulds Isolated from Different Sources*, "American Journal of Animal and Veterinary Sciences", vol. 9, no. 4, pp. 303–314.

38 T. Steviæ, T. Beriæ, K. Šavikin, M. Sokoviæ, D. Goðevac, I. Dimkiæ, S. Stankoviæ, (2014), *Antifungal Activity of Selected Essential Oils against Fungi Isolated from Medicinal Plant*, "Industrial Crops and Products", vol. 55, pp. 116–122.

39 O. Niculescu, M. Leca, Z. Moldovan, D.C. Deselnicu, (2015), *Obtaining and Characterizing of a Product with Antifungal Properties Based on Essential Oils and Natural Waxes for Finishing Natural Leathers*, "Revista de Chimie – Bucharest", vol. 66, no. 11, pp. 1733–1736.

40 E.E. Bayramoðlu, G. Gülümser, I. Karaboz, (2008), *The Investigation of Antibacterial Activities of Some Essential Oils in Wet Blue Leather*, "International Journal of Natural and Engineering Sciences", vol. 2, no. 1, pp. 33–36.

2.3. Modification of Footwear Materials By Means of Natural and Safe Substances of Antibacterial and Antifungal Properties

Essential oils have become an integral part of everyday life. They are used in a great variety of ways: as food flavouring, as feed additives, as flavouring agents in the tobacco industry, and in the compounding in cosmetics and perfumes. Furthermore, they are used in air fresheners and deodorisers as well as in all branches of medicine such as in pharmacy, balneology, massage, and homeopathy. Aromatherapy and aromachology represent a more specialised area. In recent years, the importance of essential oils as biocides and insect repellents has led to a more detailed study of their antimicrobial potential. Essential oils are also good natural sources of substances proving commercial potential as input materials for chemical synthesis.[41]

2.3.1. Safety of cinnamon, peppermint and oregano essential oils in the context of toxic effects on human health and the natural environment. Comparison with commercial preparations

A quantitative and qualitative analysis of the essential oils oregano (Bamer), cinnamon bark, peppermint (Essence) was carried out. In order to demonstrate the safety of the essential oils, it was checked whether their ingredients were classified as hazardous under the CLP (classification, labelling, packaging) Regulation, i.e. REGULATION (EC) No 1272/2008 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/200. The regulation aims to protect human health and the natural environment. For comparison, the ingredients of commercially available preparations for the preservation of leather, textiles and polymeric materials were analysed in the same way. The results are shown in Tables 2.4 to 2.6.

41 E. Schmidt, (2020), *Production of essential oils*, [in:] K. Hüsnü Can Başer, G. Buchbauer (eds), *Handbook of Essential Oils*, CRC Press, Boca Raton, p. 36.

Table 2.4. Composition and toxicity of oregano oil (Bamer) hazardous for health and the natural environment (in compliance with the CLP Regulation)

Substance/ Ingredient of the oil	Quantity [weight %]	Human Toxicity	Environmental Toxicity
pinene	0,25		
camphene	0,47		
β-pinene	1,29		
1-octen-3-ol	–		
p-cymene	4,10		
limonene	0,25	Flam. Liq. 3 Skin Irrit. 2 Skin Sens. 1 H226 H315 H317	Aquatic Acute 1 Aquatic Chronic 1 H400 H410
eucalyptol	3,87		
γ-terpinene	3,71		
linalool	4,74	Skin Sens. 1B H317	
camphor	2,49		
borneol	2,43		
4-terpineol	1,06		
α-terpineol	1,26		
thymoquinone	–		
thymol	1,11	Acute Tox. 4 * Skin Corr. 1B H302 H314	Aquatic Chronic 2 H411
carvacrol	59,41		
caryophyllene	9,91		
humulene	1,66		
unidentified	1,99		

Source: own elaboration.

Table 2.5. Composition and toxicity of cinnamon bark oil (Essence, Turkey) hazardous for health and the natural environment (in compliance with the CLP Regulation)

Substance/ Ingredient of the oil	Quantity [weight %] Cinnamon Essence (bark)	Quantity [weight %] Cinnamon Turkey (bark)	Human Toxicity	Environmental Toxicity
1	2	3	4	5
pinene	2,98	0,69		
camphene	–	0,33		

Table 2.5 (cont.)

1	2	3	4	5
benzaldehyde (almond oil)	0,71	–	Acute Tox. 4 H302	
β-pinene	1,40	0,30		
felandren	–	0,82		
cymene	2,86	1,31	Flam. Liq. 3 Skin Irrit. 2 Skin Sens. 1 H226 H315 H317	Aquatic Acute 1 Aquatic Chronic 1 H400 H410
eucalyptol	4,63	1,85		
γ-terpinene	1,09	–		
linalool	9,04	10,77	Skin Sens. 1B H317	
isoborneol	–	–		
4-terpineol	0,51	–		
α-terpineol	3,23	0,18		
cinnamaldehyde	49,42	61,07		
isosafrole	–	–		
safrole*	–	–	Carc. 1B Muta. 2 Acute Tox. 4 H350 H341 H302	
carvacrol	–	–		
p-eugenol	–	–		
α-terpinyl acetate	1,70	–		
eugenol*	1,80	5,32		
dimethyl acetal of cinnamaldehyde	0,79	–		
caryophyllene	11,52	11,27		
cinamyl acetate	0,69	2,94		
benzyl benzoate	0,04	–	Acute Tox. 4 H302	Aquatic Chronic 2 H411
unidentified	7,59	3,15		

Source: own elaboration.

Table 2.6. Composition and toxicity of peppermint oil (Essence) hazardous for health and the natural environment (in compliance with the CLP Regulation)

Substance/ Ingredient of the oil	Quantity [weight %] Mint (Essence)	Quantity [weight %] Mint (Turkey)	Human Toxicity	Environmental Toxicity
1	2	3	4	5
pinene	0,01	0,57		
β-pinene	0,02	0,89		
myrcene	–	–		
3-octanol	0,05	0,05		
limonene	0,23	–	Flam. Liq. 3 Skin Irrit. 2 Skin Sens. 1 H226 H315	Aquatic Acute 1 Aquatic Chronic 1 H317 H400 H
linalool	0,10	–	Skin Sens. 1B H317	
trans-p-mentha-2,8-dien-1-ol	0,04	–		
isopulegol	0,15	–		
isomentone	0,40	0,21		
menthone	23,59	8,38		
levomenthol	1,98	15,58		
trans-1,3-cis-1,4-menthol	19,56	11,51		
menthol	42,57	36,29		
terpinen-4-ol	–	–		
α-terpineol	1,26	0,75		
cis-dihydrocarvone	–	–		
trans-dihydrocarvone	–	–		
trans-carvone	–	–		
pulegone*	0,30	0,43		
carvone	–	–	Skin Sens. 1 H317	
piperitone	1,40	0,82		
menthol acetate	0,66	7,29		
element	0,18	0,10		
bourbonene	0,54	0,30		
longifolene	0,10	0,06		

Table 2.6 (cont.)

1	2	3	4	5
copaene	0,47	0,08		
isogermacrene	0,49	–		
germakren	0,13	0,21		
γ-cadinene	0,04	0,03		
δ-cadinene	0,11	0,08		
unidentified	5,90	16,69		

Source: own elaboration.

In Tables 2.7 to 2.9 the abbreviations used are explained in accordance with the CLP Regulation.

Table 2.7. Hazard Class and Category Code (human)

Hazard Class and Category Code (Human)	
Acute Tox. 4	Acute toxicity
Carc. 1B	Carcinogenicity
Flam. Liq. 3	Flammable liquid
Muta. 2	Germ cell mutagenicity
Skin Corr. 1B	Skin corrosion/irritation
Skin Irrit. 2	Skin corrosion/irritation
Skin Sens. 1	Respiratory/skin sensitisation
Skin Sens. 1B	Respiratory/skin sensitisation

Source: own elaboration according to the CLP Regulation.

Table 2.8. Hazard Class and Category Code (Natural Environment)

Hazard Class and Category Code (Natural Environment)	
Aquatic Acute 1	Posing a risk to the aquatic environment
Aquatic Chronic 1	
Aquatic Chronic 2	

Source: own elaboration according to the CLP Regulation.

Table 2.9. Physical, Health and Environmental Hazard Statements

Physical Hazard Statements	
H226	Flammable Liquid and Vapour
Health Hazard Statements	
H302	Harmful if swallowed.
H314	Causes severe skin burns and eye damage.
H315	Irritates the skin.
H317	May cause an allergic skin reaction.
H341	Suspected of causing genetic defects <state the route of exposure if it is definitively proven that no other route of exposure causes risk>.
H350	May cause cancer <state the route of exposure if it has been definitively proven that no other route of exposure causes the hazard>.
Environment Hazard Statements	
H400	Very toxic to aquatic organisms.
H410	Very toxic to aquatic organisms with long-lasting effects.
H411	Very toxic to aquatic organisms with long-lasting effects.

Source: own elaboration according to the CLP Regulation.

Essential oils are natural substances with multidirectional effects. There are numerous compounds in their composition, including unidentified ones. As it can be seen from the list above, most of them are completely safe and have no adverse impact on either human health or the natural environment. A few can affect human health (causing mainly skin irritation) and the natural environment, but are found in essential oils in very small quantities (tables above), which means that essential oils have no adverse impact on health and the natural environment and are completely safe.

Tables 2.10.–2.40. exhibit the composition and human and environmental toxicity of commercial preparations for the modification of leather, textiles and polymers to impart antimicrobial properties.

Table 2.10. Composition and toxicity of Sanitized T 27-22 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
Silver chloride	2	–	–

Source: Safety data sheet for Sanitized T 27-22.

Table 2.11. Composition and toxicity of Sanitized T 28-28M hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
Silver chloride	1,35	–	–

Source: Safety data sheet for Sanitized T 28-28M.

Table 2.12. Composition and toxicity of Sanitized TH 22-27 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
zinc pyrithione CAS:13463-41-7	15	Repr. 1B, H360D, Acute Tox. 2, H330, Acute Tox. 3, H301, STOT RE 1, H301, Eye Dam. 1, H318	Aquatic Acute 1, H400, Aquatic Chronic 1, H410

Source: Safety data sheet for Sanitized TH 22-27.

Table 2.13. Composition and toxicity of Sanitized T 99-19 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
Dimethyltetradecyl [3-(trimethoxysilyl)-propyl]ammonium chloride CAS: 27668-52-6	50	–	–

Source: Safety data sheet for Sanitized T 99-19.

Table 2.14. Composition and toxicity of Ultra-Fresh DW-30 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
Tiabendazole (2-(4-Thiazolyl)-1H-benzimidazole) CAS:148-79-8	15	–	Aquatic Acute 1, H400, Aquatic Chronic 1, H410
zinc pyrithione (Bis(1-hydroxy-2(1H)-pyridinethionato-O,S)-(T-4) zinc) CAS:13463-41-7	15	Repr. 1B, H360D, Acute Tox. 2, H330, Acute Tox. 3, H301, STOT RE 1, H301, Eye Dam. 1, H318	Aquatic Acute 1, H400, Aquatic Chronic 1, H410

Source: Safety data sheet for Ultra-Fresh DW-30.

Table 2.15. Composition and toxicity of Ionpure hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
Silver-zinc-aluminium-boron phosphate glass/ silver-zinc oxide glass	100	–	–

Source: Safety data sheet for Ultra-Fresh DW-30.

Table 2.16. Composition and toxicity of Dezyntol [*antifungal and antibacterial agent*] hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
Quaternary ammonium compounds, benzyl-C8-18-alkyldimethyl, chlorides 2 of the quaternary ammonium compounds (benzylalkyldimethyl (alkyl from C8-C22 saturated and unsaturated, tallow alkyl, coco alkyl and soya alkyl), chlorides, bromides, or hydroxides CAS:63449-41-2	5	Acute Tox. 4, H312 Acute Tox. 4, H302, Skin Corr. 1B, H314	Aquatic Acute 1, H400

Source: Safety data sheet for Dezyntol.

Table 2.17. Composition and toxicity of Acticide SR2405 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
2-Octyl-2H-isothiazole-3-one CAS:26530-20-1	6 g/100 g	Acute Tox. 2, H330, Acute Tox. 3, H311, Acute Tox., H313, Skin Corr. 1, H314, Eye Dam. 1, H318, Skin Sens. 1 A, H317	Aquatic Acute 1, H400, Aquatic Chronic 1, H410

Source: Safety data sheet for Acticide SR2405.

Table 2.18. Composition and toxicity of Acticide WB 300 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
2(Thiocyanomethylthio) benzothiazole CAS:2156-17-0	> 25%	Acute Tox. H330, Acute Tox. 4 H302, Acute Tox. 4 H312, Skin Irrit.2 H315, Eye Irrit 2 H319, Skin Sens 1 H317	Aquatic Acute 1 H400, Aquatic Chronic 1 H410
Benzenesulfonic acid, 4-C10-14-alkyl derivs, calcium salts	1–3%	Eye Dam. 1 H318, Skin Irrit.2 H315	Aquatic Chronic 3, H412

Source: Safety data sheet for Acticide WB 300.

Table 2.19. Composition and toxicity of Acticide WB 920 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
2-octyl-2H-isothiazol-3-one CAS:26530-20-1	20%	Acute Tox.3 H311, Acute Tox. 3 H331, Skin Corr. 1B H314, Eye Dam. 1 H318, Acute Tox.4 H302, Skin Sens. 1A H317	Aquatic Acute 1 H400, Aquatic Chronic 1 H410
Ethoxylated fatty alcohol	< 2,5%	Eye Dam. 1 H318	

Source: Safety data sheet for Acticide WB 920.

Table 2.20. Composition and toxicity of Busan 85 hazardous for health and the natural environment Busan 85 (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
Potassium dimethyldithiocarbamate CAS:128-03-0	50 g/100 g	–	–

Source: Safety data sheet for Busan 85.

Table 2.21. Composition and toxicity of N-Silveria Quattro hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
Silver CAS:7440-22-4	12%	–	–

Source: Safety data sheet for N-Silveria Quattro.

Table 2.22. Composition and toxicity of Ultracide FFOB hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
2-octyl-2H-isothiazol-3-on CAS: 26530-20-1	45	Acute Tox.3 H311, Acute Tox. 3 H331, Skin Corr. 1B H314, Eye Dam. 1 H318, Acute Tox.4 H302, Skin Sens. 1A H317	Aquatic Acute 1 H400, Aquatic Chronic 1 H410

Source: Safety data sheet for Ultracide FFOB.

Table 2.23. Composition and toxicity of NSP-200 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
Silver CAS:7440-22-4	1,27–3,17	–	–

Source: Safety data sheet for NSP-200.

Table 2.24. Composition and toxicity of NSP-100 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
Silver CAS: 7440-22-4	0,2–0,5	–	–

Source: Safety data sheet for NSP-100.

Table 2.25. Composition and toxicity of Parmetol S15 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
4,5-Dichloro-2-octyl-2H-isothiazol-3-one CAS:64359-81-5	10%	Acute Tox. 2, H330, Acute Tox. 4, H302, Skin Corr. 1, H314, Eye Dam. 1, H318, Skin Sens. 1 A, H317	Aquatic Acute 1, H400, Aquatic Chronic 1, H410

Source: Safety data sheet for Parmetol S15.

Table 2.26. Composition and toxicity of Proxel BD20 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
1,2-Benzisothiazol-3(2H)-one CAS: 2634-33-5	20	Acute Tox. 4, H302, Skin Irrit. 2, H315, Eye Dam. 1, H318, Skin Sens. 1, H317	Aquatic Acute 1, H400

Source: Safety data sheet for Proxel BD20.

Table 2.27. Composition and toxicity of Reputex 20 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
Poly(hexamethylenebicyanoguanide-hexamethylenediamine) hydrochloride CAS:27083-27-8	20	Carc. 2, H351, Acute Tox. 2, H330, Acute Tox. 4, H302, STOT RE 1, H372, Eye Dam. 1, H318, Skin Sens. 1B, H317	Aquatic Acute, H400, Aquatic Chronic 1, H410

Source: Safety data sheet for Reputex 20.

Table 2.28. Composition and toxicity of Irgaguard F 3610 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
2-thiazol-4-yl-1H-benzoimidazole (also called thiabendazole) CAS: 148-79-8	5–15	–	Aquatic Acute 1, H400, Aquatic Chronic 1, H410

Source: Safety data sheet for Irgaguard F 3610.

Table 2.29. Composition and toxicity of Irgaguard B 1000 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
5-Chloro-2-(2,4-dichlorophenoxy) phenol (also called triclosan) CAS: 3380-34-5	100	Eye Irrit. 2, H319 Skin Irrit. 2, H315	Aquatic Acute 1, H400, Aquatic Chronic 1, H410

Source: Safety data sheet for Irgaguard B 1000.

Table 2.30. Composition and toxicity of Sodium 2-Phenylphenol sodium salt S30 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
Aqueous solution of 2-phenylphenol sodium salt CAS:132-27-4	30	Acute Tox. 4, H302, STOT SE 3, H335, Skin Irrit. 2, H315, Eye Dam. 1, H318,	Aquatic Acute 1, H400

Source: Safety data sheet for Sodium 2-Phenylphenol sodium salt S30.

Table 2.31. Composition and toxicity of P&T230 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
Titanium (IV) oxide CAS: 13463-67-7	5%	Carc. 2, H351	–

Source: Safety data sheet for P&T230.

Table 2.32. Composition and toxicity of Slimicide T hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
2H-1,3,5-Thiadiazine-2-thione, tetrahydro-3,5-dimethyl (also called 3,5-Dimethyl-perhydro-1,3,5-thiadiazine-2-thione)	99	–	–

Source: Safety data sheet for Slimicide T.

Table 2.33. Composition and toxicity of Germin KF hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
sodium 4-chloro-3-methylphenol	> 20	–	–
2-hydroxybiphenyl sodium salt CAS:132-27-4	7–25	Acute Tox. 4, H302, STOT SE 3,H335, Skin Irrit. 2, H315, Eye Dam. 1, H318,	Aquatic Acute 1, H400

Source: Safety data sheet for Germin KF.

Table 2.34. Composition and toxicity of Acticide TE hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
N-1H-Benzimidazol-2-yl-carbamic Acid Methyl Ester (Carbendazim) CAS:10605-21-7	2,5–10	Muta. 1B, H340, Repr. 1B, H360FD,	Aquatic Acute 1, H400, Aquatic Chronic 1, H410

Source: Safety data sheet for Acticide TE.

Table 2.35. Composition and toxicity of Acticide SR8282 hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
zinc pyrithione CAS:13463-41-7	2,5–10	Repr. 1B, H360D, Acute Tox. 2, H330, Acute Tox. 3, H301, STOT RE 1, H301, Eye Dam. 1, H318	Aquatic Acute 1, H400, Aquatic Chronic 1, H4100
N-1H-Benzimidazol-2-yl-carbamate Acid Methyl Ester (Carbendazim) CAS:10605-21-7	2,5–10	–	–

Source: Safety data sheet for Acticide SR8282.

Table 2.36. Composition and toxicity of Metasol TK 100LC hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
Thiabendazole CAS:148-79-8	20	–	Aquatic Acute 1, H400, Aquatic Chronic 1, H410

Source: Safety data sheet for Metasol TK 100LC.

Table 2.37. Composition and toxicity of Proxel GXL Antimicrobial hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
1,2-benzoisothiazolin -3-one CAS:2634-33-5	20%	Acute Tox. 4, H302, Skin Irrit. 2, H315, Eye Dam. 1, H318, Skin Sens. 1, H317	Aquatic Acute 1, H400
Dipropylene glycol CAS:25265-71-8	–	–	–

Source: Safety data sheet for Proxel GXL.

Table 2.38. Composition and toxicity of Proxel GXL Preservative hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
1,2-benzoisothiazolin-3-one CAS:2634-33-5	20%	Acute Tox. 4, H302, Skin Irrit. 2, H315, Eye Dam. 1, H318, Skin Sens. 1, H317	Aquatic Acute 1, H400
Dipropylene glycol	–	–	–

Source: Safety data sheet for Proxel GXL.

Table 2.39. Composition and toxicity of Preventol U-Tec G (DE) hazardous for health and the natural environment (in compliance with the CLP Regulation)

Active Substance	Quantity [weight %]	Human Toxicity	Environmental Toxicity
1	2	3	4
2-Phenylphenol CAS:90-43-7	30–50	Skin Irrit. 2 H315; Eye Irrit. 2 H319, STOT SE 3 H335,	Aquatic Acute 1 H400, Aquatic Chromic 1 H410

Table 2.39 (cont.)

1	2	3	4
Chlorocresol CAS: 59-50-7	30–50	Acute Tox. 4 H302, Skin Corr. 1C H314, Eye Dam. 1 H318, Skin Sens. 1B H335	Aquatic Acute 1 H400, Aquatic Chromic 3 H412
2-Octyl-2H-isothiazol-3-one CAS:26530-20-1	5–10	Acute Tox. 4 H302, Acute Tox. 3 H331, Acute Tox. 3 H311, Skin Corr. 1B H314, Eye Dam. 1 H318, Skin Sens. 1 H317	Aquatic Acute 1 H400, Aquatic Chromic 1 H410

Source: Safety data sheet for Preventol U-Tec G (DE).

Explanation of the abbreviations used in accordance with the Regulation:

Table 2.40. Hazard class and category code (human and natural environment)

Hazard class and category code (human)	
Acute Tox.	Acute toxicity
Acute Tox. 2	
Acute Tox. 3	
Acute Tox. 4	
Carc. 2	carcinogenicity
Muta. 1B	Mutagenic effect on germ cells
Skin Corr. 1	Skin corrosion/irritation
Skin Corr. 1B	
Skin Corr. 1C	
Skin Irrit. 2	Skin corrosion/irritation
Skin Sens. 1	Respiratory/skin sensitisation
Skin Sens. 1A	
Skin Sens. 1B	
Repr. 1B	Reproductive toxicity
Eye Dam. 1	Serious eye damage/irritation
Eye Irrit. 2	
STOT RE 1	Toxic effects on target organs
STOT SE 3	

Hazard class and category code (natural environment)	
Aquatic Acute 1	Posing a risk to the aquatic environment
Aquatic Chronic 1	
Aquatic Chronic 2	
Aquatic Chronic 3	

Source: own elaboration according to CLP Regulation.

Table 2.41. Health and environmental hazard statements

Health hazard statements	
H301	Toxic if swallowed.
H302	Harmful if swallowed.
H311	Toxic by skin contact.
H312	Harmful in contact with skin.
H314	Causes severe skin burns and eye damage.
H315	Skin irritation.
H317	May cause an allergic skin reaction.
H318	Causes serious eye damage.
H319	Eye irritation.
H330	There is a risk of death if inhaled.
H331	Toxic if inhaled.
H335	May cause irritation of the respiratory tract.
H341	Suspected of causing genetic defects <state the route of exposure if it is definitively proven that no other route of exposure causes risk>.
H350	May cause cancer <state the route of exposure if it is definitively proven that no other route of exposure causes the hazard>.
H351	May cause cancer <state the route of exposure if it is definitively proven that no other route of exposure causes the hazard>.
H360D	May be harmful to the child in the womb.
H360FD	May cause reproduction damage. May be harmful to the child in the womb.
H372	Causes damage to organs <state all known organs affected > through prolonged or repeated exposure <state the route of exposure if other routes of exposure are proven not to be hazardous>.

Table 2.41 (cont.)

Environmental hazard statement	
H400	Very toxic to aquatic organisms.
H410	Very toxic to aquatic organisms with long-lasting effects.
H411	
H412	

Source: own elaboration according to CLP Regulation.

Chemicals used for preserving fibre, leather, rubber and polymerised materials have diverse health and environmental effects depending on the concentration and type of active substance, as shown in the tables above. Commercial preparations, which contain the above-mentioned chemicals, are intended for the preservation of fibre, leather, rubber and polymerised materials and are officially approved for use.

When compared to essential oils, the chemicals in the formulations have far greater adverse impact on human health and the natural environment.

Only a few constituents of the oils show skin irritation: carvone, linalool, limonene, cymene.

Oregano oil made by Bamer contains 18 substances and 1.99% of them are unidentified. It contains thymoquinone, for which no percentage is given, and only three components have an effect on human health: limonene, linalool, thymol, and only two – on the aquatic environment: limonene and thymol.

Essence Company Cinnamon Bark Oil – 23 constituents and 7.59% of them remain unidentified, proving no concentration of camphene, phellandrene, isoborneol, isosafrole, safrole, carvacrol, and p-eugenol, out of which only 5 may have adverse impact on human health and 4 – on the aquatic environment.

Essence peppermint oil contains 30 ingredients and 5.9% of them remain unidentified, out of which only 3 substances are classified in the CLP Regulation as hazardous to human health (limonene, linalool, carvone) and only one is regarded as hazardous to the natural environment (limonene).

In commercial chemical preparations, the ingredients are chemicals that adversely affect human health and the natural environment and prove high concentration ranging from 1–100%. In addition, some of those substances are classified in the CLP Regulation as hazardous, not only causing skin irritation, e.g. 2-phenylphenol contained in Preventol U-Tec G, proving its concentration of 30–50%. In addition to adverse effects on skin, namely Skin Irritation 2 H315, it also causes Eye Irritation 2 H319, and causes the target organ effect: STOT SE 3 H335, and is additionally toxic to the natural environment: Aquatic Acute 1 H400, Aquatic Chromic 1 H410.

In Proxel GXL Preservative and Proxel GXL Antimicrobial, 1,2-benzoisothiazolin-3-one as the active ingredient is contained at the concentration of 20% and exhibits acute toxicity: Acute Tox. 4, being harmful if swallowed H302, and may cause skin and eye irritation or damage: Skin

Irritation 2, H315, Eye Damage 1, H318, Skin Sensitivity 1, H317. Moreover, the so-called isothiazolinones (1,2-benzisothiazolinone-3-one and 2-methyl-4-isothiazolin-3-one) cause contact allergy and have been withdrawn from "leave-on" cosmetic products (e.g. creams), being permitted in "rinse-off" cosmetic products (shampoos) and in construction and household chemicals.

In Acticide TE the active ingredient is 2-octyl-2H-isothiazol-3-one (2.5–10%) that may have mutagenic effects on germ cells Muta. 1B, H340 and reproductive toxicity Repr. 1B, may impair fertility and may cause harm to the unborn child H360FD. The hazard classification of the chemical components of commercial preparations used for preserving fibre, leather, rubber and polymerised materials is much more hazardous than that of the components of essential oils, and besides, the concentrations of substances that can cause hazards are incomparably higher. Only preparations containing silver: Sanitized T27-22 and Sanitized 28-28M, are not hazardous and have no effects on human health and the natural environment according to the CLP Regulation. However, silver and its compounds, especially in the nano size, can migrate through human cell membranes and consequently deposit in internal organs. Silver Nanoparticles derived from, for example, antiseptic dressings has been shown to migrate into the blood[42] and cause toxic effects on cells and organs[43] in result of entering the body through various routes. Therefore, the safety of its use is limited. Furthermore, by separating from the substrate, it migrates into water bodies where it adversely impacts the development of flora and fauna.

Essential oils are mixtures of compounds that cause far less impact on human health and the natural environment than commercial preparations containing synthetic chemicals. The constituents in essential oils that may adversely impact health and the natural environment are found in small quantities and may mainly cause skin irritation. Chemicals in commercial preparations used for preserving leather, fibre, and polymers are found in high concentration and, in addition to skin irritation, may cause more serious consequences, such as harmful effects on fertility, harmful effects on the unborn child. In addition to their function, that can also be achieved through the use of chemical synthetic preparations (antimicrobial), essential oils impart an aromatic function to the modified material, which is definitely an added value.

One of the objectives of the Cornet Project "Development of microbiologically active, user and environment friendly materials for the light industry" was to develop a method for microencapsulating essential oils and applying the resulting

42 A. Bacciarelli, M. Kołodziejczyk, E. Rybicki, (2008), *Wpływ nanocząstek srebra na funkcjonowanie organizmu człowieka*, Materiały seminaryjne z XXIX Seminarium Polskich Kolorystów.

43 J. Zhang, F. Wang, S.S.K. Yalamarty, N. Filipczak, Y. Jin, X. Li, (2022), *Nano Silver-Induced Toxicity and Associated Mechanisms*, "International Journal of Nanomedicine", vol. 26, no. 17, pp. 1851–1864.

microencapsulations to light industry materials. During the project, it was shown that cinnamon oil has suitable antibacterial and antifungal properties for the protection of footwear materials. It inhibits the growth of micro-organisms and does not disturb the normal microflora of the foot's skin and was therefore selected for further work as a safe substance with no adverse impact on the natural environment or human health.

Cinnamon oil is extracted from cinnamon (Cinnamomum zeylanicum and Cinnamon cassia – a tropical tree belonging to the Lauraceae family) by means of steam distillation. It has a delicate, slightly sweet fragrance and is characterised by its strong antiseptic action. It may be used for preventing foot and nail fungus. In addition, it disinfects and kills skin-unfriendly bacteria. Promotes skin regeneration in cases of inflammation and reduces it.[44]

Footwear manufacturers, in order to meet consumer demands, are constantly looking for functional innovation that may account for a quality product upgraded with additional functions. The encapsulation of active substances including essential oils is the process that will give footwear materials new functions, such as antimicrobial, repellent, fragrance, extended performance, among others. Furthermore, the choice of ingredients used for modifying the materials arising from a group of natural substances that are safe for the environment and the user is an added value that fits in the global environmental and climate protection policy, a part of which is the use of raw materials from renewable sources.

Essential oils being the core of the capsule and mixtures of biopolymers, e.g. polysaccharides and proteins as the envelope, are ideal raw materials derived from renewable sources,[45, 46, 47] which will provide the modified material with additional functions without adversely affecting the natural environment or human health.

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44 G.R. Mallavarapu, S. Ramesh, R.S. Chandrasekhara, B.R.P. Rao, P.N. Kaul, A.K. Bhattacharya, (1995), *Investigation of the essential oil of cinnamon leaf growth at Bangalore and Hyderabad*, "Flavour and Fragrance Journal", vol. 10, pp. 239–242.

45 N. Devi, M. Sarmah, B. Khatun, T. Maji, (2017), *Encapsulation of active ingredients in polysaccharide-protein complex coacervates*, "Advances in colloid and interface science", vol. 239, pp. 136–145.

46 M. Semenova, (2017), *Protein-polysaccharide associative interactions in the design of tailor made colloidal particles*, "Current Opinion in Colloid and Interface Science", vol. 28, pp. 15–21.

47 C. Michon, F. Vigouroux, P. Boulenguer, G. Cuvelier, B. Launay, (2000), *Gelatin/iota carrageenan interactions in non-gelling conditions*, "Food hydrocolloids", vol. 14, no. 3, pp. 203–208.

2.4. Encapsulation as a method of extending the activity of active ingredients applied to light industry materials

2.4.1. Basic Encapsulation Concepts

The encapsulation process involves the entrapment of a substance (active substance) in a carrier material (wall material). The encapsulated material can be referred to as the core, filling, active, internal or loading phase. The encapsulating material is generally referred to as a coating, membrane, envelope, capsule, carrier material, outer phase or matrix.

Encapsulation is defined as a technology in which the active ingredient is contained in a core surrounded by a polymer matrix that produces a capsule.[48]

The purpose of encapsulation is to:

- protect the active compound from environmental factors (light, temperature, moisture, inappropriate pH, etc.) that affect the stability and stability of the active substance,
- release the active compound in a controlled manner at a specific pH and temperature so that the active compound acts at its intended location,
- facilitate the handling of the active compound due to the protection provided by the polymeric matrix,
- reduce or eliminate the unpleasant taste or odour of the active compound or any of the core materials,
- reduce the volatility of the active ingredient.

Many special properties can be imparted to materials through the application of microcapsules, the core of which may be any substance that fulfils specific functions, e.g. antibacterial, antifungal, repellent, therapeutic, moisturising, aromatising, or anti-inflammatory. The quality of microcapsules is influenced by many factors, including preparation techniques, core types and types of wall material.[49] [50] [51] [52]

48 S. Rani, A. Goel, (2021), *Microencapsulation technology in textiles: A review study*, "The Pharma Innovation Journal", vol. 10, no. 5, pp. 660–663.

49 B.B. Podgornik, S. Šandríc, M. Kert, (2021), *Microencapsulation for Functional Textile Coatings with Emphasis on Biodegradability—A Systematic Review*, "Coatings", vol. 11, no. 11, p. 1371.

50 A. Tulshyan, E. Dedhia, (2021), *An overview of microencapsulation technology in the application of aroma and antibacterial finishes*, "International Journal of Home Science", vol. 7, no. 1, pp. 34–39.

51 S. Bansode, S. Banarjee, D. Gaikwad, S. Jadhav, R. Thorat, (2010), *Microencapsulation: A review*, "International Journal of Pharmaceutical Sciences Review and Research", vol. 1, no. 2, p. 43.

52 A. Chanana, M.K. Kataria, M. Sharma, A. Bilandi, (2013), *Microencapsulation: Advantages in applications*, "International Research Journal of Pharmacy", vol. 4, no. 2, pp. 1–5.

Based on the size of the capsules or particles produced, encapsulation is referred to as microencapsulation and nanoencapsulation. Each has specific features that distinguish them from one another.

Microencapsulation is defined as the encapsulation into particles between 1 μm and 1000 μm in size. Microencapsulation is characterised by a prolonged, gradual release of the active ingredient, allowing for the effect to persist over a longer period of time.

Nanocapsules typically have a particle size of 50 nm to 500 nm, and have a larger surface area for the same volume. Due to their small size, nanocapsules can be easily and homogeneously distributed in liquids. Micro- and nanoencapsulation are usually used for encapsulating a single active compound.[53, 54, 55, 56, 57]

2.4.2. Microencapsulation Techniques

The most commonly used microencapsulation techniques include lyophilisation, spray drying and coacervation.

Lyophilisation involves drying at low temperature, usually below 40°C. It is used for active compounds and encapsulating materials that are temperature-sensitive.[58] Lyophilisation reduces the degradation of the core and matrix substances and increases the encapsulation efficiency of the active compound. In this technique, the encapsulating materials and active compounds are homogenised in an aqueous solution until they are fully hydrated, then the solution is lyophilised. Microencapsulates obtained by freeze-drying are characterised by the lack of size uniformity and a smooth surface, which, according to some authors, may hinder the release of active substances.[59]

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53 E. Assadpour, S.M. Jafari, (2019), *Advances in spray-drying encapsulation of food bioactive ingredients: from microcapsules to nanocapsules*, "Annual Review of Food Science and Technology", vol. 10, pp. 103–131.

54 B. Prakash, A. Kujur, A. Yadav et al., (2018), *Nanoencapsulation: an efficient technology to boost the antimicrobial potential of plant essential oils in food system*, "Food Control", vol. 89, pp. 1–11.

55 Y.P. Timilsena, T.O. Akanbi, N. Khalid et al., (2019), *Complex coacervation: principles, mechanisms and applications in microencapsulation*, "International Journal of Biological Macromolecules", vol. 121, pp. 1276–1286.

56 R. Pisano, A. Arsiccio, L.C. Capozzi et al., (2019), *Achieving continuous manufacturing in lyophilization: technologies and approaches*, "European Journal of Pharmaceutics and Biopharmaceutics", vol. 142, pp. 265–279.

57 S.A. Mahdavi, S.M. Jafari, E. Assadpoor et al., (2016), *Microencapsulation optimization of natural anthocyanins with maltodextrin, gum Arabic and gelatin*, "International Journal of Biological Macromolecules", vol. 85, pp. 379–385.

58 M. Przybysławska, K. Winnicka, (2012), *Technologie otrzymywania mikrokapsułek*, „Farmacja Polska", vol. 68, no. 4, pp. 283–289.

59 Rani, S., Goel A., (2021), *Microencapsulation technology…*

Spray drying involves drying at high temperature, generally above 100°C, to convert a liquid solution into microencapsulated powder of controlled size and morphology. The disadvantage of using spray drying is that it can damage the active compound and the encapsulating materials, mainly due to the high temperature in the drying chamber. Therefore, when choosing a spray drying technique for microencapsulation, it is necessary to evaluate and select the ideal temperature for the process. Spray drying is a continuous and economical process that produces dry particles of good quality and is carried out in spray dryers that are now widely available.[60]

Coacervation is the most commonly used microencapsulation technique. This process involves the separation of phases in a colloid or polymer solution and the formation of two or more liquid phases. The 'rich' colloid phase is the coacervate. Phase separation occurs under the influence of a change in temperature, pH or salt addition. Due to the way the process is carried out, a distinction is made between simple and complex coacervation.[61]

Simple coacervation involves a single envelope material, using gelatine as an example. The process involves combining an aqueous gelatine solution with an alcoholic oil solution under appropriate mixing parameters and temperature. The microcapsules are precipitated with acetone or through addition of e.g. sodium sulphate, which facilitates the formation of a polymeric envelope around the core.[62] Simple coacervation is achieved by changing the parameters that cause molecular dehydration of macromolecules, e.g. temperature change, pH change, through addition of ions or insoluble substances. The core should be compatible with the carrier and insoluble in the coacervation environment.

Complex coacervation is a method using two types of wall materials with opposite ionic charges. By mixing the two wall materials, their solubility is reduced due to the mutual attraction of positive and negative charges, which solidify and precipitate, and the core material is encapsulated. This method is typically used for encapsulating liquid substances susceptible to oxidative degradation. The main compounds used for complex coacervation are polysaccharides and proteins,[63] both of which are polymers with opposite charges that form the envelope.

The complex coacervation process consists of 5 steps: polymer dissolution, emulsion, coacervation, curing and rinsing/filtering/drying.

Among the parameters that can change during the coacervation process are: pH, temperature, ionic strength of each encapsulating material, compatibility of the

60 S.G. Bayryamov, (2020), *Microencapsulation of natural oils by a coacervation technique using gelatin as shell material*, "Journal of Chemical Technology and Metallurgy", vol. 55, no. 6, pp. 1985–1989.

61 Y.P. Timilsena, T.O. Akanbi, N. Khalid et al., (2019), *Complex coacervation…*

62 C.E. Sing, (2017), *Development of the modern theory of polymeric complex coacervation*, "Advances in Colloid and Interface Science", vol. 239, pp. 2–16.

63 N. Devi, M. Sarmah, B. Khatun, T. Maji, (2017), *Encapsulation of…*

encapsulating material, concentration of each encapsulating material, amount of salts possibly added, homogenisation rate of the encapsulating materials and active compound. All these variables have an impact on the performance of the process, so it is necessary to investigate the optimal conditions for each encapsulating material.[64] [65]

The authors of the study emphasise that, once the encapsulation methodology is developed, compound coacervation is highly reproducible, scalable, economical, does not require highly specialised equipment and allows for high encapsulation efficiencies of the active compound (> 99%), thus reducing wastage.

The choice of microencapsulation method depends on specific applications and parameters, such as the required particle size, physicochemical properties of the core and coating materials, release mechanisms, process cost, etc.[66]

2.4.3. Encapsulating/Coating Materials

Coating materials are substances that are used for ensuring the appropriate structure of microcapsules. The characteristics of an ideal encapsulating material for a microcapsule include: biodegradability, non-reactivity with the core material (chemical inertness), ability to tightly retain the core inside the capsule, ability to form maximum protection of the core against adverse factors (moisture, light, temperature, oxygen, etc.), plasticity. The most commonly used encapsulating materials are mainly natural and synthetic polymers, such as starch, dextrins, sucrose, cellulose, chitosan, gum arabic, alginate, carrageenan. They can also include fatty substances such as paraffin, waxes, monoglycerides and diglycerides, hydrogenated oils and fats, as well as inorganic materials such as calcium sulphate and silicates, and proteins such as gluten, casein, gelatine and albumin. The capsule shell is made up of one or more of the substances listed above.

Gelatine is a protein material obtained by partial hydrolysis of collagen. Depending on the type of hydrolysis carried out, a different type of gelatine is produced. Type A gelatine is obtained by acid hydrolysis, mainly from pig skin, and type B gelatine is obtained by alkaline hydrolysis, mainly from animal bones and skin.[67] Typically, gelatine is used for microencapsulating bioactive compounds by means of coacervation in combination with polysaccharides[68] e.g. alginate, carrageenan.

Carrageenans constitute a family of linear, sulphated polysaccharides (galactans) extracted from marine organisms – the red algae, Gigartinales.

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64 L. Lin, J.M. Regenstein, S. Lv et al., (2017), *An overview of gelatin derived from aquatic animals: properties and modification*, "Trends in Food Science & Technology", vol. 68, pp. 102–112.

65 N. Devi, M. Sarmah, B. Khatun, T. Maji, (2017), *Encapsulation of…*

66 S.G. Bayryamov, (2020), *Microencapsulation of…*

67 L. Hilliou, (2021), *Structure-Elastic Properties Relationships in Gelling Carrageenans*, "Polymers", vol. 13, no. 23, p. 4120.

68 C. Michon, F. Vigouroux, P. Boulenguer, G. Cuvelier, B. Launay, (2000), *Gelatin/iota carrageenan…*

There are three types of carrageenan most commonly used: kappa (κ), iota (ι) and lambda (λ), having two and three sulphate ester groups. Among them, κ-carrageenin is the most commonly produced and used due to its high gelling ability caused by the C4 conformation of 3,6-anhydro-D-galactopyranosyl, which forms a helix-like structure. The formation of the helix structure is facilitated by the huge number of -OH groups that form many hydrogen bonds. The commercial importance of carrageenans results from their thermo-reversible gelling ability.[69] The electrostatic interaction between gelatine and ι-carrageenan in aqueous solutions, at pH below the isoelectric point of the protein, leads to the formation of polyelectrolyte complexes through complex coacervation.[70, 71]

Chitosan is a linear polysaccharide obtained by deacetylation of chitin. Chitin is a naturally occurring polymer found in the shells of shrimps and other crustaceans. The structure of chitosan consists of a deacetylated part (β-(1,4)-D-glucosamine) and an acetylated part (N-acetyl-D-glucosamine).

Chitosan owes its wide range of applications to its safety, non-toxicity, biocompatibility, biodegradability and other unique properties, such as its film-forming ability and antimicrobial activity. Those properties provide for a broad spectrum of chitosan applications: antimicrobial/antifouling coatings, controlled-release coatings and microcapsules, hydrogels for drug delivery, and tissue engineering.[72]

Alginate is a polysaccharide extracted from marine algae, mainly brown algae (Phaeophyceae).[73] Alginates are naturally occurring polysaccharide copolymers consisting of ß-D-mannuronic (M-blocks) and α-L-guluronic acid (G-blocks) residues linked together by glycosidic bonds. The interaction of alginates with divalent cations, especially Ca^{2+}, leads to the formation of gels. The distinctive molecular structure resulting from those interactions is defined by the 'eggs-box' model ('egg in an egg-box' or 'egg stamping'), where homopolymeric G-blocks form three-dimensional ordered regions in which Ca2+ ions are embedded like eggs in a cardboard box.[74] Immediate gelation of alginate, when combined with

69 M.A.R.D. Fauzi et al., (2021), *Preparation, Properties and Potential of Carrageenan-Based Hard Capsules for Replacing Gelatine: A Review*, "Polymers", vol. 13, no. 16, p. 2666.

70 P.S. Bakshi, D. Selvakumar, K. Kadirvelu, (2020), *Chitosan as an environment friendly biomaterial – a review on recent modifications and applications*, "International Journal of Biological Macromolecules", vol. 150, pp. 1072–1083.

71 H.H. Tonnesen, J. Karlsen, (2002), *Alginate in drug delivery system*, "Drug Development and Industrial Pharmacy", vol. 28, no. 6, pp. 621–630.

72 N. Emmerichs, J. Wingender, H.-C. Flemming, C. Mayer, (2004), *Interaction between alginates and manganese cations: identification of preferred cation binding sites*, "International Journal of Biological Macromolecules", vol. 34, pp. 73–79.

73 J. Tu, S. Bolla et al., (2005), *Alginate microparticles prepared by spray-coagulation method: preparation, drug loading and release characterization*, "International Journal of Pharmaceutics", vol. 303, no. 1–2, pp. 171–181.

74 Q. Cheng, L. Yan, (2005), *Nonwoven substrate finishing with essence microcapsules,* "AATCC Review", vol. 8, pp. 46–48.

calcium ions, results in the formation of particles with diverse diameters and porosity.[75] Alginate microcapsules containing essential oil have been applied to non-woven fabrics used as substrates in the production of synthetic leather.[76]

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of glucopyranose units linked by α-(1,4)-acetal bonds. Commonly used natural cyclodextrins are α-, β- and γ-cyclodextrins consisting of 6, 7 and 8 glucopyranose units, respectively. Cyclodextrin molecules have a unique structure with a hydrophobic cavity and a hydrophilic surface that can form an inclusion complex with guest compounds. This property allows for cyclodextrins to be used in microencapsulation processes. Studies have shown that this method is one of the most effective options to ensure the protection of active compounds from oxidation, thermal degradation or evaporation.[77]

2.4.4. Release Methods

Release from microcapsules may be planned and triggered by external stimuli:

- rupture of the microcapsule wall under mechanical stress, using external pressure;
- diffusion of the substance constituting the microcapsule core after degradation of the wall, caused by chemicals or enzymes, by external factors, e.g. temperature, pH level, light;
- extraction of the microcapsule core material by placement in a suitable solvent;
- rupture of the microcapsule wall by swelling of the core substance.

While the rate of release of the substance contained in the microcapsule depends on:

- the type of polymer from which the wall is formed;
- the thickness of the wall;
- the diameter of the microcapsule.

If the microcapsules are bonded to the fibrous structure with a binding agent, the release of the contents of the microcapsules depends not only on the parameters of the microcapsule but also on the properties of the agent.[78, 79, 80]

75 J.F. Ayala-Zavala, H. Soto-Valdez, A. González-León et al., (2008), *Microencapsulation of cinnamon leaf (Cinnamomum zeylanicum) and garlic (Allium sativum) oils in b-cyclodextrin*, "Journal of Inclusion Phenomena and Macrocyclic Chemistry", vol. 60, pp. 359–368.

76 S. Jothi Sri et al., (2012), *Microencapsulation: A Review*, "International Journal of Pharma and Biosciences", vol. 3, no. 1, pp. 509–531.

77 A. Valdes, M. Ramos, (2018), *Recent Trends in Microencapsulation for Smart and Active Innovative Textile Products*, "Current Organic Chemistry", vol. 22, no. 12, pp. 1237–1248.

78 B.B. Podgornik, S. Šandríc, M. Kert, (2021), *Microencapsulation for…*

79 B. Boh, E. Knez, (2006), *Microencapsulation of essential oils and phase change materials for applications in textiles products*, "Indian Journal of Fibre and Textile Research", vol. 31, no. 1, pp. 72–82.

80 N. Singh, J. Sheikha, (2020), *Microencapsulation and its application in production of functional textiles*, "Indian Journal of Fibre & Textile Research", vol. 45, pp. 495–509.

2.4.5. Application of Microcapsules to Light Industry Materials

Published studies reveal several technologies for the incorporation of microcapsules into materials. The most common way is to disperse microcapsules in a binding agent and then apply this dispersion to a fabric (non-woven or knitted fabric) by means of various techniques: surfacing, coating, laminating, printing, nozzle spraying.[81, 82, 83, 84, 85, 86]

The disadvantage of using a bonding agent is that the performance of the products may be impaired. To ensure a permanent bond to the fibre structure, the amount of bonding agent used must be sufficiently large. However, a large amount of binding agent increases the stiffness of the fabric, deteriorates its grip, reduces air permeability and water vapour permeability, and reduces thermal resistance. The binding agent may also interfere with the controlled release of the active substance.

Microcapsule walls coated with a binding agent may offer too much resistance to wear and tear. The layer of binding agent may also interfere with the release of the active substance from the microcapsule when the wall is torn.

A method of bonding microcapsules to the fibre surface analogous to the fibre/reactive dye bond is sometimes used. In order to achieve such a bond, the polymer from which the encapsulant is formed must have reactive groups capable of forming covalent bonds with functional groups of the fibre polymer (e.g. with a hydroxyl group in the case of cellulosic fibre). This way of linking microcapsules to the fibre structure ensures more effective control of the release of the active substance from the textile product. The microcapsules obtained by polycondensation at the interface are immobilised by chemical bonding after modification of the envelope surface. It is possible to chemically bind microcapsules to the fibre of natural and synthetic polymers. This method of incorporating microcapsules into fibre does not require the use of binding agents. The bonding of microcapsules to the textile remains permanent even after 20 washes.

Another method of incorporating microcapsules into a fibre structure involves integrating microcapsules into the matrix of the polymer from which the fibre is formed. Fibre containing microcapsules is currently manufactured, the components

81 A. Tulshyan, E. Dedhia, (2021), *An overview of…*

82 Rani, S., Goel A., (2021), *Microencapsulation technology…*

83 A. Nadi, A. Boukhriss, A. Bentis, E. Jabrane, S. Gmouh, (2018), *Evolution in the Surface Modification of Textiles: A Review*, "Textile Progress", vol. 50, pp. 67–108.

84 B. Boh Podgornik, M. Starešiníc, (2016), *Microencapsulation Technology and Applications in Added-Value Functional Textiles*, "Physical Sciences Reviews", vol. 1, no. 1, pp. 20150003.

85 M. Starešiníc, B. Šumiga, B. Boh, (2011), *Microencapsulation for Textile Applications and Use of SEM Image Analysis for Visualisation of Microcapsules*, "Tekstilec", vol. 54, pp. 80–103.

86 G. Nelson, (2002), *Application of Microencapsulation in Textiles*, "International Journal of Pharmaceutics", vol. 242, pp. 55–62.

of which are the so-called phase change materials (PCMs), i.e. materials capable of changing their state of aggregation within a certain temperature range called the phase change temperature. They are used for manufacturing the so-called 'smart textiles' that have a thermoregulatory effect due to the absorption or emission of heat depending on the temperature change.

In the process of manufacturing functional textiles, microencapsulation aims to improve properties or impart new functionalities, resulting in broader usability and higher added value of products.

The main functionalities achieved by microencapsulation in textile coatings *inter alia* include thermochromic and photochromic effects, flame retardancy, improved thermal regulation, UV absorption, insecticidal and insect repellent effects, prolonged fragrance release, antimicrobial properties.

The Functionalisation of textiles with microcapsules containing natural essential oils (EOs) is an ecological solution. Those exhibit a broad spectrum of antimicrobial and biological activity and, depending on their chemical composition, can exhibit repellent, antibacterial, antifungal, UV-protective and other properties.

Manufacture of environmentally friendly biodegradable textiles containing biodegradable microcapsules is one of the biggest challenges for textile functionalisation research.

The physical and chemical properties of microencapsulation methods based on natural polymers (chitosan, gum arabic and gelatine or biodegradable synthetic polymers such as PLA) have been used for the purpose of the research, the outcome of which has been published so far.

In the textile industry, microcapsules can be applied to fibre, yarn and fabric-based techniques such as impregnation, spray, pad-dry-cure and screen printing.

One of the main obstacles to the widespread use of biodegradable microcapsules in functional textiles is their unsatisfactory durability and resistance to washing, wiping and light, which are crucial for textile care and sustainable functionality.

Further research should focus on the possibility of introducing new biodegradable materials as microcapsule envelopes and coating compositions with improved property technology or the use of functional groups on the microcapsule envelope to allow covalent bonds to be formed with the functional groups of biodegradable textiles, so that higher adhesion between microcapsule and fibre can be achieved.

For textile applications, essential oils can be encapsulated through simple coacervation with e.g. gum arabic,[87] ethyl cellulose[88] or through complex

87 R. Sharma, A. Goel, (2018), *Development of insect repellent finish by a simple coacervation microencapsulation technique*, "International Journal of Clothing Science and Technology", vol. 30, no. 2, pp. 152–158.

88 G.C. Türkoğlu, A.M. Sariişik, G. Erkan, H. Kayalar, O. Kontart, S. Öztuna, (2017), *Determination of antioxidant capacity of capsule loaded textiles,* "Indian Journal of Fibre & Textile Research", vol. 42, pp. 189–195.

coacervation with e.g. chitosan/gum arabic,[89, 90] gelatine/gum arabic,[91] gelatine/carboxy cellulose.[92]

Few companies offer microcapsules dedicated to textiles in order to ensure the presence of active substances with a specific effect. Textiles modified with microcapsules of a suitable composition allow for a prolonged, slow or controlled release of active substances, the possibility of transferring those active substances to the skin, and the possibility of immobilising the capsules on the fibres.

In the leather industry, many additives and functional agents are known which, when applied to the skin, effectively perform their functions. Such additives, depending on their nature, can be applied using a number of different processes depending on the type of functional preparation. As in the case of textiles, the effective long-lasting effect of functional additives dedicated to leather can be achieved by encapsulating them.[93]

In the footwear industry, the incorporation of encapsulated antimicrobial substances into leather materials or components will allow for the creation of active footwear, which will contribute to improvement of user comfort, satisfaction of customer needs and expectations by eliminating odours generated during footwear use, incorporating controlled odour release chemical substance or preventing degradation and improving durability.

Buket et al.[94] showed that orange oil microparticles obtained by spray drying and applied to leather shoe insoles exhibited natural antibacterial properties.

2.4.6. Development of the Microencapsulation Method for Cinnamon Oil

Essential oils are volatile compounds with a core coating that slows down their release, prolonging their effect.

Preliminary studies were carried out to select the most favourable composition of the cinnamon oil microcapsule matrix in terms of form and encapsulation

89 A. Sharkawy, I.P. Fernandes, M.F. Barreiro, A.E. Rodrigues, T. Shoeib, (2017), *Aroma-Loaded Microcapsules with Antibacterial Activity for Eco-Friendly Textile Application: Synthesis, Characterization, Release, and Green Grafting*, "Industrial & Engineering Chemistry Research", vol. 56, no. 19, pp. 5516–5526.

90 M.M. Sánchez-Navarro, M.Á. Pérez-Limiñana, F. Arán-Ais, C. Orgilés-Barceló, (2015), *Scent properties…*

91 F.M. Bezerra, O.G. Carmona, C.G. Carmona, M.J. Lis, F.F. de Moraes, (2016), *Controlled release of microencapsulated citronella essential oil on cotton and polyester matrices*, "Cellulose", vol. 23, no. 2, pp. 1459–1470.

92 M.Á. Pérez-Limiñana, F.J. Payá-Nohales, F. Arán-Ais, C. Orgilés-Barceló, (2013), *Effect of the shell-forming polymer ratio on the encapsulation of tea tree oil by complex coacervation as a natural biocide*, "Journal of Microencapsulation", vol.31, no. 2, pp. 176–83.

93 R. Painter, US-6685746-B1, *Impregnation of leather with micro-encapsulated material*.

94 B. Yılmaz, H.A. Karavana, (2020), *Application of Chitosan-Encapsulated Orange Oil onto Footwear Insock Leathers*, "Johnson Matthey Technology Review", vol. 64, no. 4, p. 443.

efficiency. The microcapsules were prepared through a complex coacervation method derived from published but modified methods.

The following polymer blends were selected for testing:

- a mixture of gelatine A and K-carrageenan;
- a mixture of gelatine A and K-carrageenan and calcium chloride;
- a mixture of gelatine and gum arabic;
- a mixture of chitosan and gum arabic;
- β-cyclodextrin.

The analysis of the microencapsulation methods has proven a variety of encapsulation efficiencies and microencapsulation shapes depending on the matrix used. The images obtained from the microscope highlight the different structure of the microcapsules obtained and suggest that they may have diversified mechanical resistance. The microscopic image of the capsules containing dextrin as a matrix (Figure 2.1.) illustrates that the powder particles have irregular shapes and diversified size, which may result in lower mechanical strength.

The image of the microcapsules with the gelatine/carrageenan/$CaCl_2$ matrix reveals spherical structures largely assembled into agglomerates (Figure 2.2.). The most favourable capsules have been obtained with the gelatine/carrageenan matrix (Figure 2.3.). They have the smallest size, spherical, regular and smooth shapes, and the highest yield of 72% has been obtained with this process. This method had been selected for optimisation that was followed by the reproducibility and efficiency test on an enlarged scale.

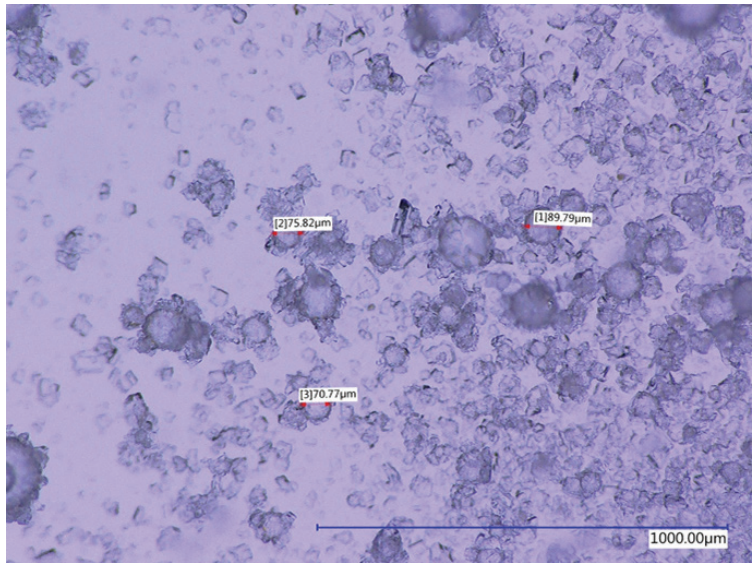

Figure 2.1. Microcapsules characteristic of the β-cyclodextrin content as the encapsulating material (Keyence digital microscope)
Source: own elaboration.

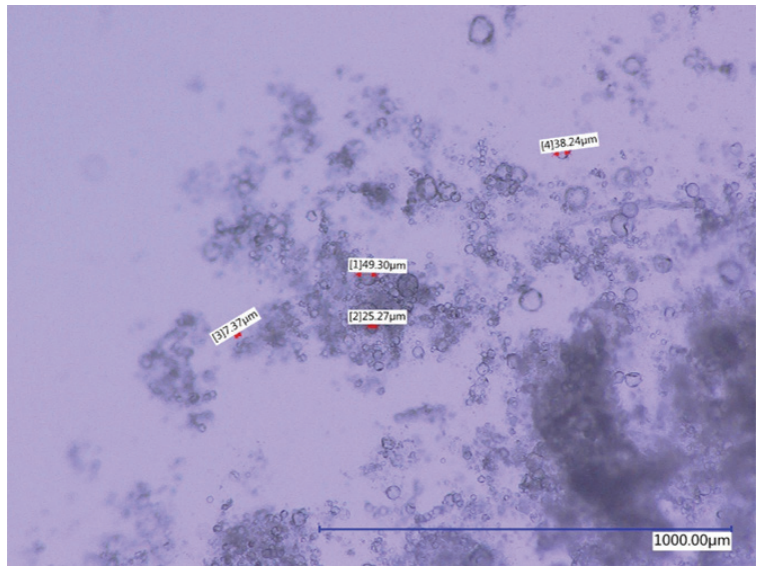

Figure 2.2. Microcapsules characteristic of the gelatine/carrageenan/$CaCl_2$ content as encapsulating material (Keyence digital microscope)
Source: own elaboration.

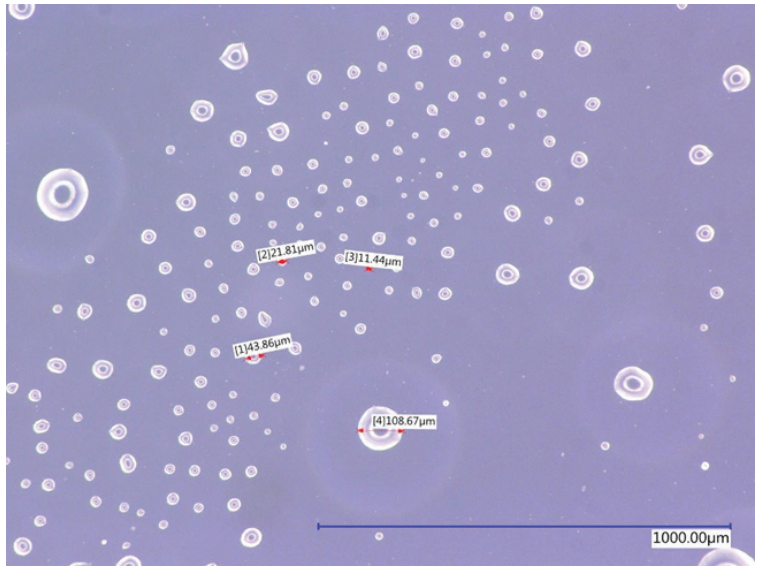

Figure 2.3. Microcapsules characteristic of the gelatine/carrageenan content as the encapsulating material (Keyence digital microscope)
Source: own elaboration.

As part of the optimisation study, the encapsulation of cinnamon oil, using gelatine/carrageenan as the matrix, has been carried out under diverse conditions set by varying the polymer and oil content with the physico-chemical parameters (volume, temperature, pH, mixing, homogenisation and separation conditions) in the preliminary study.

General Synthetic Procedure

5, 10, 15 ml of cinnamon oil was dispersed at 50°C in a solution of 50 ml in volume containing 2.5 g of gelatine. The mixture was stirred by means of a mechanical stirrer at the stirring rate of 400 rpm at 50°C for 30 min to produce a stable oil-in-water emulsion.

250 ml of 0.2 or 0.5% carrageenan solution at 45–50°C and pH = 7 adjusted with 1M NaOH solution was added into the produced emulsion.

Maintaining a constant temperature of 50±2°C, the emulsion was stirred at the stirring rate of 400 rpm for 15 min. The pH of the emulsion was then brought to 4.0 by adding a 1 M HCl solution to stabilise the polymers. At this pH value, gelatine was positively charged and k-carrageenan negatively charged. To allow for coacervation, the emulsion was stirred at the stirring rate of 400 rpm for 1.5 h. At the end of coacervation, the heating was turned off and 600 ml of cold deionised water was added, and the system was then cooled down to 5–10°C in an ice bath.

Under those conditions, gelatine and carrageenan surrounded the oil droplets and microcapsules were formed. Curing of the microcapsules was carried out through slow stirring for 2 h at the stirring rate of 300 rpm and storage at 4°C for 24 h.

The resulting microcapsules were filtered and washed by means of 20 ml of water.

The effect of oil loading variation, polymer concentration on microcapsule behaviour is summarised in Table 2.42.

Table 2.42. Average Values for Microencapsulation Yield and Effectiveness

Amount of Oil (g)	Amount of Gelatine (g)	K-karagen n (g)	Micro-encapsulation Yield (%)	Micro-encapsulation Effectiveness (%)	Method of Separation and Observations
5	2,5	0,5	72	51,2	Slow filtration
10	2,5	0,5	91	68,6	Very fast filtration
15	2,5	0,5	_	_	Emulsion, no phase separation
5	2,5	1,25	60	31,5	Slow filtration
10	2,5	1,25	82	46,7	Slow filtration
15	2,5	1,25	_	_	Emulsion, no phase separation

Source: own elaboration.

Within the framework of the trials conducted, the highest coacervate yields (%) were obtained with the gelatine/carrageenan encapsulating polymer weight ratio of 5:1 and the use of 10 g of oil.

Given those weight ratios and the target conditions, the interaction between the two polymers was top efficient, resulting in the maximum amount of insoluble coacervate that was produced.

2.4.7. Application of Microcapsules to Carrier Materials (Leather, Cotton)

Light industry materials (cotton fabric, wet blue leather) were used for the purpose of applying manufactured microcapsules containing cinnamon oil providing for microbiological protection.

The padding process involved Keeper cotton fabric of 260 g/m^2 in surface weight, that had been pre-washed at the boiling point in a bath containing the anionic surfactant Rokanol O18 (1g/l), and wet-blue leather of 830 g/m^2 in surface weight.

The process of applying the capsules to the fabric was carried out through batch processing by means of a Foulard laboratory surfacing machine with adjustable roller pressure.

Pre-washed cotton fabric of 10 x 25 cm in size and leather of 10 x 25 cm in size were impregnated in the in the padder at 25°C using a water bath containing gelatine-carrageenan microcapsules.

In order to evaluate the effective bioactive effect depending on the amount of microcapsules applied, surfacing baths were prepared to use three concentrations of microcapsules: 10, 20, 30 g /l.

The samples in the surfacing baths were maintained for 30 min.

They were then destained between the surfacer rollers at a pressure of the rollers allowing for a post-padding weight gain of 190–200% in relation to dry weight. After surfacing, the samples were air-dried to avoid possible damage to the microcapsules.

2.4.8. Microbiological Activity of Materials Modified with Microcapsules Containing Cinnamon Oil

The samples obtained were subjected to microbiological tests for the presence of bacteria and fungi (E.Cola, S.aureus, A.niger, C.albicans, Ch.globosum) according to the following procedures:

Procedure 1. Testing the antibacterial properties of leather and fabric surfaced with essential oil encapsulated in microcapsules against two bacterial strains.

Objective of the study: To determine the antibacterial activity of the tested leather and fabric against two bacterial strains: Escherichia coli, Staphylococcus aureus.

Test method: PN-EN ISO 20645:2006 "Flat textile products. Determination of antimicrobial activity. Diffusion method on agar plate."[95]

Principle of the method: Working samples are placed on two-layer agar plates. The lower layer contains only agar, the upper layer – agar inoculated with a bacterial suspension of a certain density. Both sides of the product are tested. After the incubation period, the zone of bacterial growth in the contact zone between the agar and the test specimen and the zone of growth inhibition around the test specimen, if found, are assessed.

Test microorganisms: Escherichia coli ATCC 8739, Staphylococcus aureus ATCC 9144.

Dimensions and number of working samples: Circular specimens of (25±5) mm in diameter were cut. Two specimens were used for each test strain for fabric-testing one side of the product due to homogeneity of the material and two specimens for each test strain for leather-testing both sides of the product.

Preparation of the bacterial suspension: Bacteria were activated by inoculation onto TSA agar medium (Tryptic Soy Agar). Agar plates were incubated 18–24h at 37±1°C. After the incubation period, bacterial suspension from the culture cultivated on TSA agar was prepared in 0.85% saline. The density of the suspension, determined densitometrically, was 0.77 McF for E. coli and 0.98 McF for S. aureus, which is within the range of 1–5x108 cfu/ml, respectively.

Performance of the assay: TSA (Tryptic Soya Agar) medium was prepared first. The medium was sterilised in an autoclave at 121°C for 30 min. It was then poured into previously prepared petri dishes. At the same time, 150 ml of TSA medium in a bottle was prepared for each test strain and inoculated with 1 ml of a fixed density bacterial suspension. The bacterial medium was poured onto the surface of the agar plates with the agar medium already solidified and the tested working samples were placed on the solidified two-layer agar. The test was carried out on both sides of the product in the case of leather, placing the specimens once with the face and once with the flesh on the agar surface. In the case of fabric, the test was carried out on one side due to the homogeneity of the material.

Incubation: Incubation was carried out for 24 h at 37°C ±1°C.

Growth assessment: Bacterial growth was assessed according to the applicable standard (Table 2.43.). Bacterial growth in the contact zone between the agar and the working sample was assessed and the zone of growth inhibition around the working sample was measured.

95 PN-EN ISO 20645:2006, *Płaskie wyroby włókiennicze. Wyznaczanie aktywności antybakteryjnej. Metoda dyfuzji na płytce z agarem*.

Table 2.43. Assessment of Bacterial Growth

Inhibition Zone	Growth	Description	Assessment
>1	lack	Inhibition zone above 1 mm, lack of growth	Good effect
1–0	lack	Inhibition zone up to 1 mm, lack of growth	
0	lack	No inhibition zone, lack of growth	
0	low	No inhibition zone, only some colonies limited in number, growth stopped almost completely	Limited efficiency
0	medium	No inhibition zone, half the increase as compared to the control group	No effect
0	strong	No inhibition zone, no reduction in growth as compared to the control group, or only a slight reduction in growth	

Source: own elaboration.

Procedure 2. Testing the antifungal properties of leather and fabric surfaced with essential oil encapsulated in microcapsules against three fungal strains.

Objective of the study: To determine the antifungal activity of the tested leather and fabric against three fungal strains: A. Niger, C. Albicans, Ch. Globosum.

Test method: PN-EN 14119:2005 Textile testing. Assessment of microfungal activity. Method B1 and method B2.[96]

Principle of the method: Working samples are treated with a standard mixture of test fungal spores on a complete agar medium (the agar medium contains a carbon source). The tested fungi can grow on the agar medium and on the article if the article has not been treated with an antifungal agent. The fungi test outcome is assessed by determining their growth rate (determination of the antifungal effect).

Test microorganisms: Aspergillus niger ATCC 6275, Candida albicans ATCC 10231, Chaetomium globosum ATCC 6205.

96 PN-EN 14119:2005, *Badania tekstyliów. Ocena działania mikrogrzybów. Metoda B1 oraz metoda B2.*

Dimensions and the number of working samples: METHOD B1: Specimens of 2.5 cm x 8 cm in size were cut and then trimmed to reach the width equivalent to 2 cm. Two specimens from each type of fabric and leather were tested. METHOD B2: Specimens of a circular shape and 30 mm in diameter were cut. Two specimens from each type of test fabric and leather were used for testing.

Preparation of the spore suspension: Fungi were activated by streaking from agar slants onto fresh Potato Dextrose Agar (PDA) plates and cultured for 6 days (29±1°C). The fungi were then streaked onto agar slants with PDA medium and incubated for 14 days at 29±1°C. The cultures prepared in this way served the basis for the spore suspension prepared by means of a solution of mineral salts ($NaNO_3$ – 2.0 g; KH_2PO_4 – 0.7 g; K_2HPO_4 – 0.3 g; KCl – 0.5 g; $MgSO_4$ x $7H_2O$ – 0.5 g; $FeSO_4$ x H_2O – 0.01 g; distilled water – 1000 ml) with a wetting agent (Tween 80). For that purpose, 5 ml of the salt solution with the wetting agent was placed in test tubes and the culture surface was gently scraped with a sterile microbiological loops. The tube was shaken to obtain an aqueous spore suspension. The suspension was then shaken with sterile glass beads and was swirled sequentially on sterile gauze pads to separate the mycelial fragments. The suspension was poured into to sterile 15 ml phalcones and centrifuged (6,000 rpm, 10 min). The supernatant was decanted and the pellet resuspended in a fresh mineral salt solution. The spores were centrifuged and washed 3 times then resuspended in 40 ml of mineral salts so that the spore concentration estimated using the Thoma Counting Chamber reached 10^6 in 1 ml.

Test Procedure:

METHOD B1: First, a complete mineral medium was prepared. For this purpose, the following salts solutions were dissolved in 1000 ml of distilled water: $NaNO_3$ – 2.0 g; KH_2PO_4 – 0.7 g; K_2HPO_4 – 0.3 g; KCl – 0.5 g; $MgSO_4$ x $7H_2O$ – 0.5 g; $FeSO_4$ x H_2O – 0.01 g. The agar added in the amount of 20g/l was then dissolved in a hot bath. Finally, glucose was added at 20 g/l. It was all sterilised in an autoclave at 121°C for 30 min. The medium was then poured into the previously prepared petri dishes. The test working samples were placed on the solidified complete agar medium. Then 0.5 ml of the spore suspension (spore suspensions of the three strains, mixed in a 1:1 ratio) was pipetted evenly onto the surface of each working sample.

METHOD B2: In respect of each separate test strain, 1 ml of spore suspension for was added to 100 ml of still liquid complete agar medium. This was mixed to distribute evenly in the agar medium in order to be poured onto the surface of petri dishes. This was allowed to solidify, after which the working samples were placed on the surface of the solidified agar.

Incubation: Incubation was carried out for 14 days at 29°C±1°C.

Growth assessment: Fungal growth was assessed according to the standard. The degree of fungal growth on the test sample as well as the zone of growth inhibition around the sample were assessed (Table 2.44.).

Table 2.44. Assessment of fungal growth on working samples

The degree of growth	Assessment
0	No visible growth assessed by microscope (50x)
1	Growth clearly visible under the microscope
2	Visible growth, covering up to 25% of the tested area
3	Visible growth, covering up to 50% of the tested area
4	Visible growth, covering more than 50% of the tested area
5	Strong growth, covering the entire tested area

Source: own elaboration.according to PN-EN 14119:2005

Table 2.45. Assessment of fungal growth on the agar around the samples

The degree of growth	Assessment
0	No visible growth assessed by microscope (50x)
1	Growth clearly visible under the microscope
2	Growth visible, intensity up to 25% of control grow
3	Visible growth, intensity up to 50% of control growth
4	Significant growth, intensity greater than 50% of control growth.
5	Strong growth, intensity the same as control growth.

Source: own elaboration according to PN-EN 14119:2005

The bioactive properties of textile (T-1, T-2, T-3) and leather (S-1, S-2, S-3) in respect of the concentration of microcapsules in the surfacing bath are shown in Table 2.46.

A very good and good microbiological and antifungal effect was achieved with as little as 10% of microcapsules in the drip. This value was assumed to be optimal for modification on an industrial scale.

Table 2.46. Microbiological activity of materials modified with microcapsules containing cinnamon oil in respect of the concentration of microcapsules in the bath

Sample	Microcapsules concentration in the bath (g/l)	Increase in weight of materials (g)	Amount of oil in capsules (g)	Bioactivity				
				E. Coli	*S. Aureus*	*A. Niger,*	*C. Albicans*	*Ch. Globosum*
1	2	3	4	5	6	7	8	9
T-1	10	8,3	6,15	Growth under sample: none Inhibition zone: 5.5 mm; Very good antibacterial effect	Growth under sample: none Inhibition zone: 7.5 mm; Very good antibacterial effect	No growth on fabric. On agar, growth covering up to 25% of the tested area. Good antifungal effect. Almost complete inhibition of growth of the test strain.	No growth on fabric and agar as assessed under the microscope (over 50x). Very good antifungal effect. Complete growth inhibition of the test strain.	No growth on fabric and agar as assessed under the microscope (over 50x). Very good antifungal effect. Complete growth inhibition of the test strain.
T-2	20	11,87	8,87	Growth under sample: none Inhibition zone: 7.0 mm; Very good antibacterial effect	Growth under sample: none Inhibition zone: 10.0 mm; Very good antibacterial effect	No growth on fabric. On agar, growth covering up to 50% of the tested area. Good antifungal effect.	No growth on fabric and agar as assessed under the microscope (over 50x). Very good antifungal effect. Complete inhibition of growth of the test strain.	No growth on fabric and agar as assessed under the microscope (over 50x). Very good antifungal effect. Complete growth inhibition of the test strain.

1	2	3	4	5	6	7	8	9
T-3	30	13,1	9,68	Growth under sample: none Inhibition zone: 9.5 mm; Very good antibacterial effect	Growth under sample: none Inhibition zone: 12.0 mm; Very good antibacterial effect	No growth on fabric and agar as assessed under the microscope (over 50x). Very good antifungal effect. Complete growth inhibition of the test strain.	No growth on fabric and agar as assessed under the microscope (over 50x). Very good antifungal effect. Complete growth inhibition of the test strain.	No growth on fabric and agar as assessed under the microscope (over 50x). Very good antifungal effect. Complete growth inhibition of the test strain.
S-1	10	5,6	4,18	Growth under sample: none Inhibition zone: Flesh 7.5 mm Face 9.0 mm Very good antibacterial effect	Growth under sample: none Inhibition zone: Flesh 6 mm Face/Grain 10 mm Very good antibacterial effect	No growth on fabric. On agar, growth covering up to 50% of the tested area. Good antifungal effect.	No growth on fabric and agar as assessed under the microscope (over 50x). Very good antifungal effect. Complete growth inhibition of the test strain.	No growth on fabric and agar as assessed under the microscope (over 50x). Very good antifungal effect. Complete growth inhibition of the test strain.
S-2	20	7,42	5,52	Growth under sample: none Inhibition zone: Flesh 10 mm Face 8.5 mm Very good antibacterial effect	Growth under sample: none Inhibition zone: flesh 8.5 mm Face 10.5 mm Very good antibacterial effect	No growth on fabric. On agar, growth covering up to 25% of the tested area. Good antifungal effect. Almost complete inhibition of growth of the test strain.	No growth on fabric and agar as assessed under the microscope (over 50x). Very good antifungal effect. Complete growth inhibition of the test strain.	No growth on fabric and agar as assessed under the microscope (over 50x). Very good antifungal effect. Complete growth inhibition of the test strain.

Table 2.46 (cont.)

1	2	3	4	5	6	7	8	9
S-3	30	9,5	7,00	Growth under sample: none Inhibition zone: Flesh 14.5 mm Face 11.5 mm Very good antibacterial effect	Growth under sample: none Inhibition zone: Flesh 13.5 mm Face 14.0 mm Very good antibacterial effect	No growth on fabric and agar as assessed under the microscope (over 50x). Very good antifungal effect. Complete growth inhibition of the test strain.	No growth on fabric and agar as assessed under the microscope (over 50x). Very good antifungal effect. Complete growth inhibition of the test strain.	No growth on fabric and agar as assessed under the microscope (over 50x). Very good antifungal effect. Complete growth inhibition of the test strain.

Source: own elaboration.

2.4.9. Durability of Carrier Materials Modified by Means of Microcapsules

Tests were also carried out on the durability of microcapsule-modified carrier materials. Samples of modified knitwear and leather were weighed and placed in a Pol Eko KKS 115 Top plus climate chamber-temperature 35°C and relative humidity 50%. Exposure time of the samples was 24 hours. The content of active substances that remained on the carrier was then examined by means of the solvent extraction and the chromatographic analysis (GC-MS). The values were related to the spray-modified samples – the content of the applied oil identical to that of the oil in the microcapsules – calculated on the basis of the microencapsulation efficiency, the concentration of the microcapsules in the surfacing bath, and the weight gain of the materials after the application process. The study shows that cinnamaldehyde remained in both the spray-modified sample and the microcapsule-modified sample after the accelerated ageing processes. This was 25.84% in the leather sample, 24.05% in the fabric sample (spray method) and 43.81% in the leather sample and 76.7% in the knitted fabric sample (microcapsule modification with cinnamon oil) in relation to the amounts applied. While the results for the spray-modified samples are similar for leather and knitwear, for the microcapsule-modified samples significantly more of the active substance remained on the knitwear (the looser structure of the knitwear resulted in immobilisation of the active substance microcapsules within the fibre network). In addition, the microbiological activity of skin and knitwear modified with cinnamon oil microcapsules subjected to accelerated ageing was confirmed. In the case of the leather sample, the zone of inhibition of 4.5 mm in size was observed for Staphylococcus aureus and for Escherichia coli it was 2.5 mm in size, while in the case of the knitted fabric, the zone of 7 mm in size was observed for both Staphylococcus aureus and Escherichia coli. The samples tested also showed a very good effect against C. Albicans, Ch. Globosum and A. Niger. No growth of any of those microorganisms was observed on their surface or around the working samples. The conducted analyses demonstrated the durability of the bioactive finish of the carrier materials with cinnamon oil encapsulated in a gelatine-carrageenan microcapsule.

The research described in section 2.1.4. was funded by the National Centre for Research and Development (Poland), grant number CORNET/28/1/2020, project title “Development of microbiologically active, user and environmentally friendly materials for the light industry”.

2.5. Self-cleaning Properties of Light Industry Materials Exemplified by Cotton Fabric and Velour Leather – Inspired by Nature[97]

The self-cleaning effect is related to the following concepts developed by scientists: TiO_2-based superhydrophilic self-cleaning, lotus effect self-cleaning, gecko setae-derived self-cleaning, and underwater organisms-inspired antifouling self-cleaning. The self-cleaning mechanism depends on the superhydrophilicity or superhydrophobicity of the surface. In the case of the superhydrophilic surface, water droplets can spread and form a thin layer on the surface that washes away contaminants as it flows off. The self-cleaning mechanism caused by superhydrophobicity, as exemplified by the so-called lotus effect, is associated with the presence of numerous microtubes on the modified surface.[98] The presence of microtubes results in a smaller contact area between the surface and the water droplets, allowing the water droplets to roll over the surface, collecting the contaminants from the surface.[99, 100, 101, 102] The self-cleaning properties of the surface are of great interest due to the wide range of applications in various industries (textile, construction, sanitary appliances, car parts – car body, mirrors, photovoltaic panels, cameras, mobile phones, cosmonautics, etc.).[103] In the textile industry, self-cleaning fabric is mainly based on surface modification with TiO_2 or SiO_2 nanoparticles. One of the methods of applying nanoparticles (nano-TiO_2 or nano-SiO_2) to fabric is the sol-gel method. Nanoparticles are produced by acidic or alkaline hydrolysis in the presence of the so-called precursors. Precursors are most often organic salts of the appropriate metals (e.g. titanium isopropoxide, tetraethyl orthosilicate). The produced nanoparticles have a high surface area to volume ratio and high surface

97 I. Masłowska-Lipowicz, A. Słubik, (2023), *Novel method of obtaining textile fabrics with self-cleaning and antimicrobial properties*, "The Journal of The Textile Institute", Vol. 114:10, 1509–1517, DOI: 10.1080/00405000.2022.2131954

98 Ibidem.

99 K. Liu, L. Jiang, (2012), *Bio-Inspired Self-Cleaning Surfaces,* "Annual Review of Materials Research", vol. 42, pp. 231–263.

100 Y. Shao, J. Zhao, Y. Fan, Z. Wan, L. Lu, Z. Zhang, W. Ming, L. Ren, (2020), *Shape memory superhydrophobic surface with switchable transition between "Lotus Effect" to "Rose Petal Effect"*, "Chemical Engineering Journal", vol. 382, 122989.

101 M.S. Hasan, M. Nosonovsky, (2020), *Lotus Effect and Friction: Does Nonsticky Mean Slippery?*, "Biomimetics", vol. 5, p. 28.

102 Z. Chan-Juan, T. Dan, H. Ji-Huan, (2018), *What factors affect lotus effect?*, "Thermal Science", vol. 22, pp. 1737–1743.

103 C.H. Han, B.G. Min, (2020), *Superhydrophobic and Antibacterial Properties of Cotton Fabrics Coated with Copper Nanoparticles through Sonochemical Process*, "Fibers Polymers", vol. 21, pp. 785–791.

energy, thanks to which they show a high affinity for fabric.[104] Additionally, the use of photocatalytic nano-TiO_2 gives textile the function of photocatalytic cleaning. In this type of fabric, contamination is broken down by UV radiation.[105, 106, 107, 108]

Self-cleaning cotton fabric with dual functions of superhydrophobicity and photocatalytic activity using micro-hierarchical TiO_2 particles was developed by Pakdel. Fluorine-free coating formulations composed of flower-like particles, either TiO_2 or nitrogen-doped TiO_2, and polydimethyl siloxane (PDMS) polymer were applied to cotton fabric using a facile dip-coating method. The produced coatings on the cotton fabric were characterised by excellent superhydrophobicity with the water contact angle of 156.7° ± 1.9°. In addition, the coated fabric showed a highly efficient photocatalytic effect, breaking down absorbed stains after 30 minutes of irradiation.[109] Chauhan et al. investigated the self-cleaning efficiency of cotton fabric surface by modifying with non-fluorinated hexadecyltrimethoxysilane solution (HDTMS). This modified cotton fabric showed repellency to water and liquids with a static contact angle greater than 150° and tilt angle less than 10°,[110] while the method of obtaining a superhydrophobic coating on cotton fabric by simply immersing in TiO_2 nanoparticles and perfluorodecyltriethoxysilane solution is described in the article by Tudu and his co-workers. The obtained coating, apart from superhydrophobic and self-cleaning properties, was characterised by excellent mechanical durability, chemical and thermal stability[111] whereas the facile, mild and low-cost approach of the fabrication of self-cleaning cotton textile was proposed by Liu et al. The fabric surface was coated with pure

104 M. Krifa, C. Prichard, (2020), *Nanotechnology in textile and apparel research – an overview of technologies and processes*, "The Journal of The Textile Institute", vol. 111, pp. 1–16.

105 Z. Altangerel, B. Purev-Ochir, A. Ganzorig, T. Tsagaantsooj, G. Lkhamsuren, A. Choisuren, G. Chimed, (2020), *Superhydrophobic modification and characterization of cashmere fiber surfaces by wet coating techniques of silica nanoparticles*, "Surfaces and Interfaces", vol. 19, 100533.

106 J. Wan, L.H. Xu, H. Pan et al., (2021), *Green water-based fabrication of SiO_2-TiO_2 aerogels with superhydrophobic and photocatalytic properties and their application on cotton fabric*, "Journal of Porous Materials", vol. 28, pp. 1501–1510.

107 M. Diaa, A.G. Hassabo, (2022), *Self-Cleaning Properties of Cellulosic Fabrics (A Review)*, "Biointerface Research in Applied Chemistry", vol. 12, pp. 1847–1855.

108 Z. Wu, K. Fang, W. Chen, Y. Zhao, Y. Xu, C. Zhang, (2021), *Durable superhydrophobic and photocatalytic cotton modified by PDMS with TiO_2 supported bamboo charcoal nanocomposites*, "Industrial Crops and Product", vol. 171, 113896.

109 E. Pakdel, H. Zhao, J. Wang et al., (2021), *Superhydrophobic and photocatalytic self-cleaning cotton fabric using flower-like N-doped TiO_2/PDMS coating*, "Cellulose", vol. 28, pp. 8807–8820.

110 P. Chauhan, A. Kumar, B. Bhushan, (2019), *Self-cleaning, stain-resistant and anti-bacterial superhydrophobic cotton fabric prepared by simple immersion technique*, "Journal of Colloid and Interface Science", vol. 535, pp. 66–74.

111 B.K. Tudu, A. Sinhamahapatra, A. Kumar, (2020), *Surface Modification of Cotton Fabric Using TiO_2 Nanoparticles for Self-Cleaning, Oil-Water Separation, Antistain, Anti-Water Absorption and Antibacterial Properties*, "ACS Omega", vol. 5, pp. 7850–7860.

TiO_2 nanoparticles through a sol-gel method catalysed by glacial acetic acid and then modified by (heptadecafluoro-1,1,2,2-tetrahydrodecyl) triethoxysilane. Such a modification led to produce a surface with self-cleaning properties in relation to solid contaminants, everyday liquids, oil, and even organic pollutants, assigning a synergistic function of superhydrophobicity and photocatalysis of TiO_2 nanoparticles.[112] [113] There are also known methods for obtaining self-cleaning coatings by coating photocatalytic zinc oxide nanoparticles (nano-ZnO)[114], [115] or titanium dioxide nanoparticle (nano-TiO_2)[116] [117] [118] on cotton surfaces using the traditional dip-pad-dry-cure coating process.

2.5.1. The Method of Obtaining Textile Fabric with Self-cleaning and Antimicrobial Properties[119]

Materials

The cotton/acrylic fabric proving the grammage of 130 g/m^2 was used in this study. The polydimethylsiloxane (PDMS) prepolymer with terminal hydroxyl groups, a product from Sigma Aldrich, was used. Titanium(IV) isopropoxide from Sigma Aldrich was used for the purpose of the synthesis of TiO_2. Ethyl tetraethyl orthosilicate was used for the purpose of the synthesis of SiO_2. Aprettan N92111 from Clarchem Poland Sp. z.o.o. was used as the crosslinking agent. In order to impart antibacterial properties of textile fabric, Sanitised T 99-19 from Clarchem Poland Sp. z.o.o was used.

112 R.S. Goonetilleke, (1999), *Footwear cushioning…*

113 M. Yang, W. Liu, C. Jiang et al., (2019), *Robust fabrication of superhydrophobic and photocatalytic self-cleaning cotton textile based on TiO_2 and fluoroalkylsilane*, "Journal of Materials Science", vol. 54, pp. 2079–2092.

114 C. Zhu, J. Shi, S. Xu et al., (2017), *Design and characterization of self-cleaning cotton fabrics exploiting zinc oxide nanoparticle-triggered photocatalytic degradation*, "Cellulose", vol. 24, pp. 2657–2667.

115 V.H.T. Thi, B.K. Lee, (2017), *Development of multifunctional self-cleaning and UV blocking cotton fabric with modification of photoactive ZnO coating via microwave method*, "Journal of Photochemistry and Photobiology A: Chemistry", vol. 338, pp. 13–22.

116 I. Ahmad, C.-W. Kan, Z. Yao, (2019), *Photoactive cotton fabric for UV protection and self-cleaning*, "RSC Advances", vol. 9, pp. 18106–18114.

117 A. Nazari, (2019), *Superior Self-cleaning and Antimicrobial Properties on Cotton Fabrics Using Nano Titanium Dioxide along with Green Walnut Shell Dye*, "Fibers Polymers", vol. 20, pp. 2503–2509.

118 I. Ahmad, C.W. Kan, (2017), *Visible-Light-Driven, Dye-Sensitized TiO_2 Photo-Catalyst for Self-Cleaning Cotton Fabrics*, "Coatings", vol. 7, no 11, p. 192.

119 I. Masłowska-Lipowicz, A. Słubik, (2023), *Novel method…*

Preparation of TiO_2 colloid by sol/gel method

TiO_2 particles were obtained by means of the sol/gel method by mixing water and ethanol in a 1:1 ratio, followed by dropwise addition of 24 ml of titanium(IV) isopropoxide. The resulting mixture was then stirred for half an hour at room temperature. At this time, 0.1 M hydrochloric acid (HCl) was added dropwise to the mixture until the pH was in the range of 3–4. The acidified mixture was stirred for 24 hours.

Preparation of SiO_2 colloid by sol/gel method

SiO_2 particles suspended in the solution were obtained by mixing water and ethanol in a 1:1 ratio, and then dropwise addition of 120 ml of ethyl tetraethyl orthosilicate. The resulting mixture was stirred for half an hour at room temperature. At this time, 0.1 M HCl was added dropwise to the mixture until the pH was in the range of 3–4. The acidified solution was stirred for 24h.

Preparation and application of PDMS/TiO_2 coatings on the fabric

The PDMS solution was prepared by mixing 200 mL of acetone with 4.2 g of poly(methylhydrosiloxane) and followed by adding 0.1% Appretan N92111 used as the crosslinker. The resulting mixture was stirred at room temperature for half an hour. The mixture prepared in this way was mixed with TiO_2 colloid in a ratio of 2:1 and applied to the fabric surface with the immersion method. Then the cotton fabric was dried at 100°C.

Preparation and application of coatings with additional antibacterial properties

5% Sanitized T 99-19 antibacterial agent containing the active ingredient quaternary ammonium salt – dimethyltetradecyl [3-(trimethoxysilyl) propyl] ammonium chloride was incorporated into PDMS/TiO_2 and PDMS/SiO_2 mixtures.

2.5.2. Characterisation Methods

Spectroscopy Characterisation

The infrared spectra of the unmodified and modified fabric were developed by means of the Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with Smart Orbit ATR (Waltkam, MA, USA) diamond attachment, using the attenuated total reflectance (ATR) method. The spectra were made for the wavenumber range of 500–3900 cm^{-1}.

In order to determine the mechanism of joining the fabric with the applied finish, for fabric before and after modification with PDMS/SiO_2 and PDMS/TiO_2 infrared spectra were made (Figure 2.4.).

In the case of the spectrum for the unmodified (cotton-acrylic fabric) sample, a wide and intense peak was observed at the wavenumber from 3000 to 3600 cm^{-1}, corresponding to the stretching vibrations of the-OH groups found in cellulose and lignin. The peak at the wavenumber of 2895 cm^{-1} was related to the > C-H group found in cotton (cellulose, hemicellulose), while the peak at the wavenumber of 2936 cm^{-1} and 2165 cm^{-1} indicated the content of -CH, $-CH_2$, $-CH_3$ groups (CH stretching vibration) and nitrile group > C≡N, respectively, found in acrylic fibre. The peak at the wavenumber of 1732 cm^{-1} corresponded to the stretching vibration of the carboxyl group > C=O found in hemicellulose and acrylic fibre. Additionally, the following peaks at the wavenumber of 1428 cm^{-1} (>CH_2 group in cellulose), 1364 cm^{-1} (> CH group in the aromatic ring in cellulose polysaccharides), 1312 cm^{-1} (> CO group in the aromatic ring in cellulose polysaccharides) and 1032 cm^{-1} (C-O and -OH group in cellulose polysaccharides) are characteristic for cotton.[120, 121] After applying PDMS/SiO_2 or PDMS/TiO_2 finish, a decrease in the intensity of the peak was observed at the wavenumber of 2965 cm^{-1}, 2165 cm^{-1} characteristic for acrylic fibre and at the number of 1732 cm^{-1} and 1032 cm^{-1} characteristic for cotton. In addition, after the application of PDMS/SiO_2 or PDMS/TiO_2 finish, the appearance of new peaks was observed at the wavenumber from 1026 cm^{-1} and 1000 cm^{-1}, probably attributed to asymmetric stretching vibrations Si-O and Si-O-Si, respectively.[122, 123, 124] The band characterising the Ti-O-Ti group was probably obscured by the peak at the wavenumber of 1310 cm^{-1} characteristic for the CH group.[125]

120 E.H. Portellaa, D. Romanzinib, C.C. Angrizanib, S.C. Amicob, A.J. Zatteraa, (2016), *Influence of Stacking Sequence on the Mechanical and Dynamic Mechanical Properties of Cotton/Glass Fiber Reinforced Polyester Composites*, "Material Research", vol. 19, no 3, pp. 542–547.

121 M. Abdouss, A. Mousavi, A. Shoushtari, A. Haji, B. Moshref, (2012), *Fabrication of chelating diethylenetriaminated PAN micro- and nano-fibres for heavy metal removal*, "Chemical Industry &Chemical Engineering Quarterly", vol. 18, pp. 27–34.

122 E. Pakdel, H. Zhao, J. Wang et al., (2021), *Superhydrophobic and photocatalytic…*

123 A.G. Koozekonan, M.R.M. Esmaeilpour, S. Kalantary, A. Karimi, K. Azam, V.A. Moshiran, F. Golbabaei, (2020), *Fabrication and characterization of PAN/CNT, PAN/TiO_2, and PAN/CNT/TiO_2 nanofibers for UV protection properties*, "The Journal of The Textile Institute", vol. 112, pp. 946–954.

124 M. Hu, Z. Wu, L. Sun, S. Guo, H. Li, J. Liao, B. Wang, (2019), *Improving pervaporation performance of PDMS membranes by interpenetrating polymer network for recovery of bio-butanol*, "Separation and Purification Technology", vol. 228, no. 1, 115690.

125 S. Foorginezhad, M.M. Zerafat, (2018), *Fabrication of stable fluorine-free superhydrophobic fabrics for anti-adhesion and self-cleaning properties*, "Applied Surface Science", vol. 464, pp. 458–471.

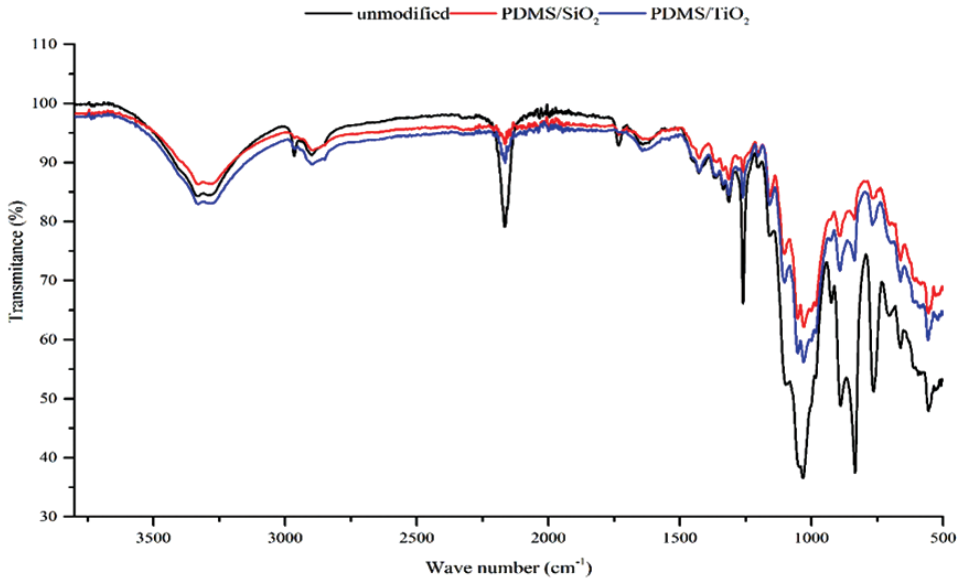

Figure 2.4. FTIR of the unmodified and modified textile fabric by PDMS/SiO_2 or PDMS/TiO_2
Source: I. Masłowska-Lipowicz, A. Słubik, (2023), *Novel method of obtaining textile fabrics with self-cleaning and antimicrobial properties*, "The Journal of The Textile Institute", Vol. 114:10, 1509–1517, DOI: 10.1080/00405000.2022.2131954

Contact Angle Measurements

The hydrophobicity of coated fabric was measured using a water contact angle meter (Phoenix-Alpha apparatus from SEO (SEO, Suwon, Korea)). A droplet of 10–3 cm^3 volume was applied to the surface of the sample with a syringe, and its photo was taken and analysed with Phoenix Alpha Contact Angle Analyzer software (SEO, Suwon, Korea). The contact angle measurements for deionised water at room temperature were performed for samples before and after application of coating. Ten contact angle measurements were conducted for each sample.

The wettability of the fabric, which is affected by the surface structure, was tested using the contact angle. The values of contact angles for the textile fabric sample before and after modification with PDMS/SiO_2 or PDMS/TiO_2 are presented in Table 2.47. and Figure 2.5. Fabric is an excellent adsorption material due to the capillary effect and high porous structure, thanks to which the liquid can be drawn into the matrix and trapped amongst the fibre.[126] Therefore, in the case of the unmodified sample, rapid absorption of the drop of water applied to the fabric was observed. However, in order to make the fabric hydrophobic, its surface was chemically modified with PDMS/SiO_2 and PDMS/TiO_2. The use of the

126 M. Adebajo, R. Frost, J. Kloprogge, O. Carmody, (2003), *Porous Materials for oil spill cleanup: A revive of synthesis and absorbing properties*, "Journal of Porous Materials", vol. 10, pp. 159–170.

proposed modifications of the surface of the textile fabric had a positive effect on the value of the contact angle and led to the formation of hydrophobic coatings, as evidenced by the value of the contact angle obtained. The contact angle for the surface modified by PDMS/SiO_2 was 147.3°, while for the surface modified by PDMS/TiO_2 was 143.5°.

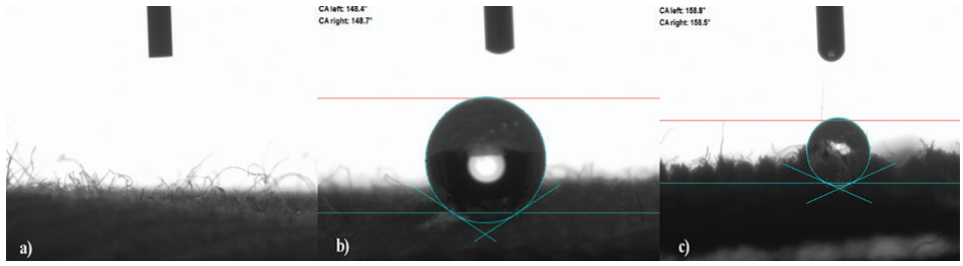

Figure 2.5. Contact angle of: a) unmodified and modified textile fabric by b) PDMS/SiO_2; c) PDMS/TiO_2
Source: I. Masłowska-Lipowicz, A. Słubik, (2023), *Novel method of obtaining textile fabrics with self-cleaning and antimicrobial properties*, "The Journal of The Textile Institute", Vol. 114:10, 1509–1517, DOI: 10.1080/00405000.2022.2131954

The durability of the obtained surface is also an important criterion for the practical application of superhydrophobic/hydrophobic surface coatings on textile fabrics. The durability of the superhydrophobic coating may result from the adhesion of SiO_2 or TiO_2 nanoparticles on the fabric surface. The durability of the surface was assessed by testing the chemical stability of the applied coatings by dipping the fabric in various solvents and water solutions with different pH values and then measuring their contact angle. The results obtained are presented in Table 2.47. The obtained PDMS/SiO_2 and PDMS/TiO_2 coatings show a very high chemical stability, as evidenced by the obtained contact angle results. The contact angle, regardless of the type of modification, increased on fabric immersed in both organic solvents (acetone, ethanol, THF) and aqueous solutions with pH 4 and pH 9. Increasing the contact angle may indicate the presence of strong chemical bonds between the fabric used and the coating layers formed.

Table 2.47. Contact angle measurement of unmodified and modified textile fabric

Sample	Contact Angle Measurement [°]
1	2
Unmodified textile fabric	a drop of water to soaked
PDMS/SiO_2	147.3
PDMS/SiO_2 (acetone)	157.3
PDMS/SiO_2 (ethanol)	155.5

1	2
PDMS/SiO_2 (THF)	154.5
PDMS/SiO_2 (pH4)	157.0
PDMS/SiO_2 (pH9)	157.3
PDMS/TiO_2	143.5
PDMS/TiO_2 (acetone)	161.3
PDMS/TiO_2 (ethanol)	156.1
PDMS/TiO_2 (THF)	153.5
PDMS/TiO_2 (pH4)	157.5
PDMS/TiO_2 (pH9)	149.2

Source: I. Masłowska-Lipowicz, A. Słubik, (2023), *Novel method of obtaining textile fabrics with self-cleaning and antimicrobial properties*, "The Journal of The Textile Institute", Vol. 114:10, 1509–1517, DOI: 10.1080/00405000.2022.2131954

Materials with a high contact angle are also self-cleaning. In the case of textile fabrics, the self-cleaning properties were assessed by applying various liquid contaminants to the fabric, and then the degree of soiling was visually assessed. Water, dye, raspberry juice, wine, and cinnamon oil were used as contaminants, and in the case of velour leather – mud. As shown in Figure 2.6. the liquid droplets on the unmodified fabric were absorbed, while on those modified by PDMS/SiO_2 or PDMS/TiO_2 coatings, the liquid droplets had a spherical shape, which proves the excellent repulsive properties of the resulting surface in relation to various types of the contamination. These liquid contamination also ran down the coated surface immediately and did not leave any dirt, unlike the unmodified fabric. In the case of applying cinnamon oil, the drops of this liquid were absorbed on both the unmodified and the modified fabric, which proves that the proposed modifications do not show oleophobic properties.

The same method was used for modifying leather – dyed velour. As shown in Figure 2.8., the mud was applied to the unmodified and modified skin. Mud composition: soil mixture taken from the residential area mixed with water in a 5:1 weight ratio. After removing the impurity, a stain remained on the unmodified leather, and there was no impurity on the modified leather.

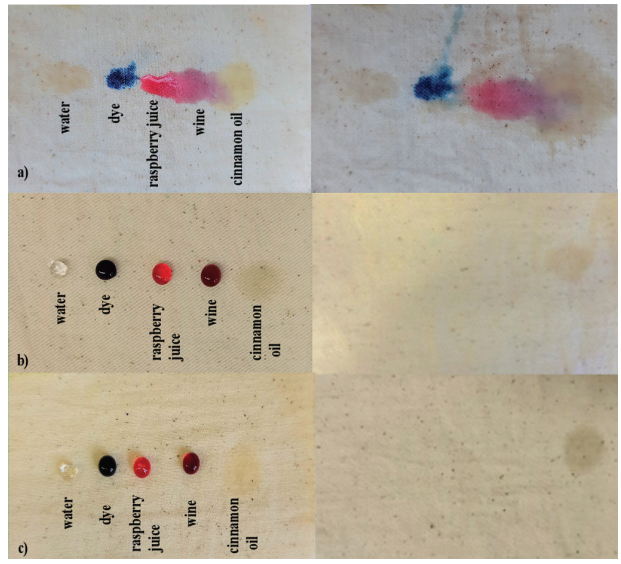

Figure 2.6. Self-cleaning properties of a) unmodified and modified textile fabric; b) PDMS/SiO_2; c) PDMS/TiO_2
Source: I. Masłowska-Lipowicz, A. Słubik, (2023), *Novel method of obtaining textile fabrics with self-cleaning and antimicrobial properties*, "The Journal of The Textile Institute", Vol. 114:10, 1509–1517, DOI: 10.1080/00405000.2022.2131954

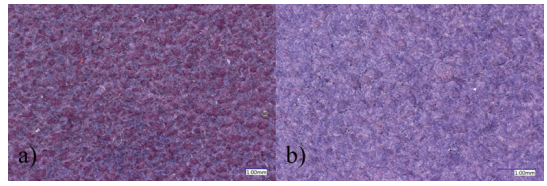

Figure 2.7. Microscopic image of velour-violet leather (a) face, (b) flesh
Source: own elaboration.

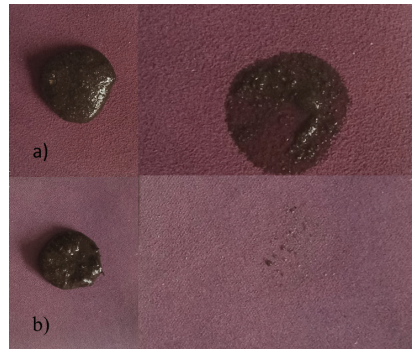

Figure 2.8. Self-cleaning properties of a) unmodified, b) modified velour leather PDMS/SiO_2
Source: own elaboration.

Antibacterial and antifungal properties of the coating

Two bacterial strains*: Escherichia coli* ATCC 8739 and *Staphylococcus aureus* ATCC 9144 were used as bacteria to test the antimicrobial properties of superhydrophobic/hydrophobic coatings on the fabric surfaces. Antibacterial tests were carried out in accordance with the PN-EN ISO 20645 standard.[127]

Two fungal strains, *Aspergillus niger* ATCC 6275, and *Candida albicans* ATCC 10231 were used as model fungi to test the antifungal properties of superhydrophobic/hydrophobic coatings on the fabric surfaces. The antifungal tests were performed in accordance with the PN-EN 14119:2005 standard.[128]

The results of testing the antibacterial activity of fabric samples against *E. coli* and *S. aureus* are presented in Table 2.48., Figure 2.9. and Figure 2.10.

Table 2.48. The results of the antibacterial activity against *E. coli* and *S. aureus* of the tested samples modified by PDMS/SiO_2 or PDMS/TiO_2

Bacterial strain	Type of sample	Growth	Inhibition zone	Description	Assessment
E. coli	PDMS/SiO_2	lack	0	No inhibition zone, lack of growth	Good effect
	PDMS/TiO_2	lack	0	No inhibition zone, lack of growth	Good effect
S. aureus	PDMS/SiO_2	lack	9.0	Inhibition zone above 1 mm, lack of growth	Good effect
	PDMS/TiO_2	lack	9.0	Inhibition zone above 1 mm, lack of growth	Good effect

Source: I. Masłowska-Lipowicz, A. Słubik, (2023), *Novel method of obtaining textile fabrics with self-cleaning and antimicrobial properties*, "The Journal of The Textile Institute", Vol. 114:10, 1509–1517, DOI: 10.1080/00405000.2022.2131954

In the case of the PDMS/SiO_2- and PDMS/TiO_2-modified fabric, in the *E. coli* test, no zone of growth inhibition around the working samples was observed. Bacterial growth directly under the fabric was not observed, either (Figure 2.4.). This means that the fabric modified with the antibacterial agent showed a good effect against *E. coli*. However, in the case of the PDMS/SiO_2- and PDMS/TiO_2-modified fabric samples, the 9.0 mm zone of growth inhibition around the samples was observed in the *S. aureus* test. There was also no growth of bacteria directly under the fabric samples (Figure 2.5.), which evidenced that the fabrics used with Sanitised T 99-19 showed a good effect against *S. aureus*. Better antibacterial effect of the PDMS/SiO_2 and PDMS/TiO_2-modified fabric was observed in the case of

127 PN-EN ISO 20645:2006, *Płaskie wyroby…*, p. 32.
128 PN-EN 14119:2005, *Badania tekstyliów…*, p. 33.

gram-positive bacteria (*S. aureus*), which is probably related to the structure of bacteria, in particular with the structure of their cell wall.

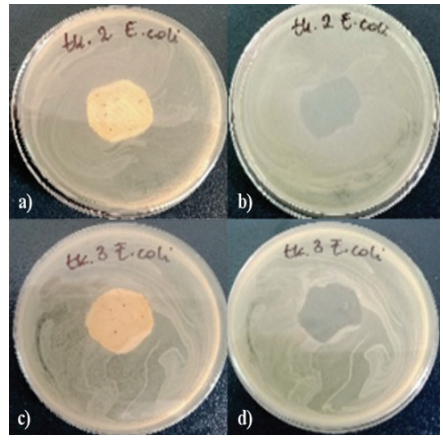

Figure 2.9. Growth of *E. coli*: a) around the PDMS/SiO_2-modified fabric; b) under the PDMS/SiO_2-modified fabric; c) around the PDMS/TiO_2-modified fabric; d) under the PDMS/TiO_2-modified fabric
Source: I. Masłowska-Lipowicz, A. Słubik, (2023), *Novel method of obtaining textile fabrics with self-cleaning and antimicrobial properties*, "The Journal of The Textile Institute", Vol. 114:10, 1509–1517, DOI: 10.1080/00405000.2022.2131954

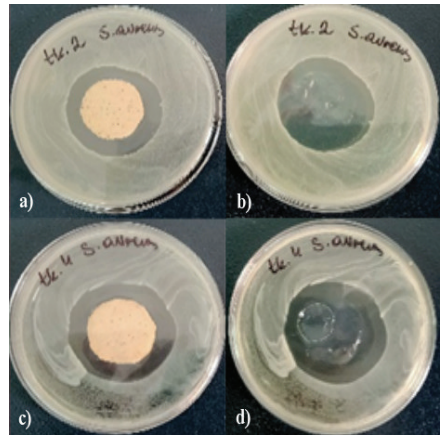

Figure 2.10. Growth of *S. aureus*: a) around the PDMS/SiO_2-modified fabric; b) under the PDMS/SiO_2-modified fabric; c) around the PDMS/TiO_2-modified fabric; d) under the PDMS/TiO_2-modified fabric
Source: I. Masłowska-Lipowicz, A. Słubik, (2023), *Novel method of obtaining textile fabrics with self-cleaning and antimicrobial properties*, "The Journal of The Textile Institute", Vol. 114:10, 1509–1517, DOI: 10.1080/00405000.2022.2131954

The results of tests of antifungal activity of the fabric samples against *Aspergillus niger* and *Candida albicans* are presented in Table 2.49.

Table 2.49. The result of the antifungal activity against *Aspergillus niger* and *Candida albicans* of the tested samples modified by PDMS/SiO_2 or PDMS/TiO_2

Fungal strain	Type of sample	Growth	Inhibition zone	Description
Aspergillus niger	PDMS/SiO_2	2	Visible growth, covering up to 25% of the tested area	Limited efficiency
	PDMS/TiO_2	2	Visible growth, covering up to 25% of the tested area	Limited efficiency
Candida albicans	PDMS/SiO_2	0	No visible growth on the fabric assessed by microscope, growth over the entire surface of the agar	Good effect
	PDMS/TiO_2	0	No visible growth on fabric assessed by microscope, minimal zone of inhibition on agar	Good effect

Source: I. Masłowska-Lipowicz, A. Słubik, (2022), *Novel method of obtaining textile fabrics with self-cleaning and antimicrobial properties*, "The Journal of the Textile Institute", https://www.tandfonline.com/doi/abs/10.1080/00405000.2022.2131954 (accessed: 09.03.2023).

Antifungal agents applied to the tested fabric had a different effect on the growth of *Aspergillus niger* and *Candida albicans*. For the fabric modified by the PDMS/SiO_2 and PDMS/TiO_2, better action against fungi was observed due to *Candida albicans* than with *Aspergillus niger*. *Candida albicans* growth was not observed on the surface of the modified fabric. For that fabric, a minimal zone of inhibition of growth around the test sample was also observed. A slightly weaker fungistatic effect of the modified fabrics was observed in the case of *Aspergillus Niger*. The growth of *Aspergillus Niger* appeared on about 25% of the tested fabric area.

The use of the proposed finish to modify the surface of the fabric made it self-cleaning. Before modification, the droplets of water and liquid impurities had been absorbed into the fabric. However, the modification resulted in obtaining hydrophobic surfaces characterised by the contact angle of about 145°. Additionally, the modified surfaces showed high durability in organic solvents and in strongly acidic and strongly alkaline solutions. The Sanitized TH 99-19 finish inhibited the growth of selected bacteria and fungi.

2.6. Auxetic Structures Used in Footwear and Clothing Materials[129]

Auxetic materials and structures have a Negative Poisson's Ratio (NPR). The Poisson's Ratio characterises the response to uniaxial stress. It is defined as the negative ratio of the transverse strain to the corresponding axial strain. The Poisson's Ratio is a dimensionless quantity>. It does not determine the elasticity of a material but the way in which it deforms. It is determined according to the following equation formula:

$$\nu = -\frac{\varepsilon_x}{\varepsilon_y} \tag{1}$$

ν – Poisson's Ratio;
ε_x – deformation along the x-axis,
ε_y – deformation along the y-axis.

Auxetics exhibit counterintuitive response. In uniaxial compression (tension), those materials and structures contract (expand) laterally.

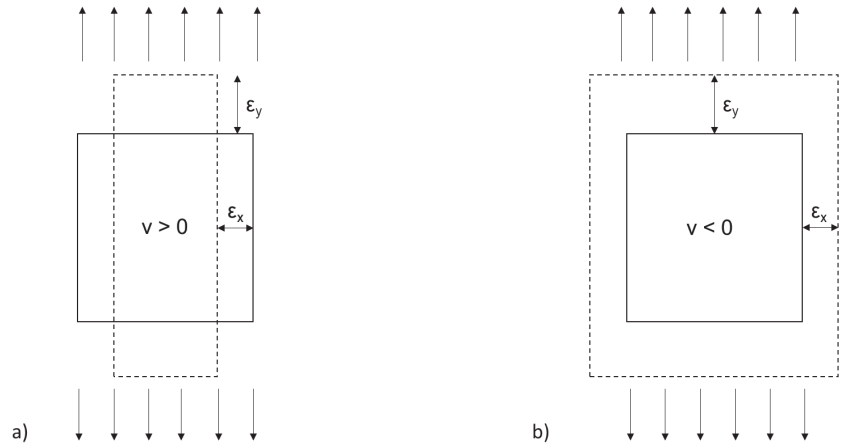

Figure 2.11. The diagram of undeformed (solid line) and deformed (dashed line):
a) conventional; b) auxetic material; ν – Poisson's Ratio; ε_x – deformation along the x-axis; ε_y – deformation along the y-axis
Source: own elaboration.

129 D. Prall, R.S. Lakes, (1997), *Properties of a chiral honeycomb with a Poisson's ratio of –1*, "International Journal of Mechanical Sciences", vol. 39, pp. 305–314.

Only few auxetic materials have been found in the natural environment. The first experimental study suggesting the existence of auxetic materials in the natural environment was reported in 1882 for iron pyrite monocrystals, the Poisson's Ratio of which was estimated to be –0.14. Other examples of natural auxetic materials include α-crystobalite, cow teat skin, pyrolytic graphite, polymorphic silicones, zeolites, silicates and crystalline cadmium.[130] [131]

The properties of materials characterised by the Negative Poisson's Ratio are for the first time mentioned in Voigt's work[132] dating back to the early 20th century. Subsequently, Lempriere[133] presented theoretical considerations for three-dimensional isotropic materials characterised by the Negative Poisson's Ratio. By and large, on the basis of the classical theory of elasticity and the thermodynamic stability of materials, the Poisson's Ratio for isotropic materials is assumed to take values within the interval (–1, 1) for the two-dimensional theory of elasticity and values within the interval (–1, 0.5) for three-dimensional materials.[134] For anisotropic materials, there are no such restrictions. In the 1980s, Gibson[135] published a paper on cellular materials inter alia containing theoretical and experimental results in respect of the materials characterised by the Negative Poisson's Ratio, and Lakes[136] presented a method for producing a synthetic foam sample showing auxetic properties.

In recent years the literature has many a time described structures, the deformation magnitude and the related Poisson's Ratio of which depend on external conditions, e.g. temperature, magnetic field, applied force or displacement.

130 R.S. Lakes, R. Witt, (2000), *Making and characterizing negative Poisson's ratio materials*, "International Journal of Metallurgical Engineering Education", vol. 30, no. 1, pp. 50–58.

131 VH. Carneiro, J. Meireles, H. Puga, (2013), *Auxetic materials – a review*, "Mater Sci – Poland", vol. 31, pp. 561–71.

132 W. Voigt, (1928), *Lehrbuch der Kristallphysik*, B. G. Teubner-Verlag, Leipzig, Berlin.

133 B.M. Lempriere, (1968), *Poisson's ratio in orthotropic materials*, "AIAA J.", vol. 6, no. 11, p. 2226.

134 K.W. Wojciechowski, (1987), *Constant thermodynamic tension Monte Carlo studies of elastic properties of a two-dimensional system of hard cyclic hexamers*, "Molecular Physics", vol. 61, p. 1247.

135 L.J. Gibson, (1981), *The elastic and plastic behaviour of cellular materials*, Churchill College, University of Cambridge, UK.

136 R.S. Lakes, (1987), *Foam structures with a negative Poisson's ratio*, "Science", vol. 235, p. 1038.

In a number of papers,[137, 138, 139, 140, 141, 142, 143] it has been shown that, by means of the above factors, the value of the Poisson's Ration can be controlled so that the structure exhibits auxetic response under certain known and controlled conditions and not under other conditions.

Short-listed models for auxetic structures

A number of research centres are investigating new deformation mechanisms leading to auxetic response with high controllability and low production costs. Representative mechanisms include re-entrant structures,[144, 145, 146, 147, 148, 149] rotating

137 I.V. Shadrivov, M. Lapine, Y.S. Kivshar (eds), (2015), *Nonlinear, Tunable and Active Metamaterials, Nonlinear, Tunable and Active Metamaterials*, Springer International Publishing, Switzerland.

138 R.S. Lakes, (2007), *Cellular solids with tunable positive or negative thermal expansion of unbounded magnitude*, "Applied Physics Letters", vol. 90, 221905.

139 R.S. Lakes, (2017), *Negative Poisson's Ratio Materials: Auxetic Solids*, "Annual Review of Materials Research", vol. 47, pp. 63–81.

140 J.N. Grima, R. Caruana-Gauci, M.R. Dudek, K.W. Wojciechowski, R. Gatt, (2013), *Smart metamaterials with tunable auxetic and other properties*, "Smart Materials and Structures", vol. 22, 084016.

141 D. Li, L. Dong, R.S. Lakes, (2016), *A unit cell structure with tunable Poisson's ratio from positive to negative*, "Materials Letters", vol. 164, pp. 456–459.

142 D. Li, J. Maa, L. Dong, R.S. Lakes, (2016), *A bi-material structure with Poisson's ratio tunable from positive to negative via temperature control*, "Materials Letters", vol. 181, pp. 285–288.

143 C.S. Ha, M.E. Plesha, R.S. Lakes, (2016), *Chiral three-dimensional lattices with tunable Poisson's ratio*, "Smart Materials and Structures", vol. 25, 054005.

144 I.G. Masters, K.E. Evans, (1996), *Models for the elastic deformation of honeycombs*, "Composite Structures", vol. 35, pp. 403–422.

145 L. Yang, O. Harrysson, H. West, D. Cormier, (2015), *Mechanical properties of 3D re-entrant honeycomb auxetic structures realized via additive manufacturing*, "International Journal of Solids and Structures", vol. 69, pp. 475–490.

146 U.D. Larsen, O. Signund, S. Bouwsta, (1997), *Design and fabrication of compliant micromechanisms and structures with negative Poisson's ratio*, "Journal of Microelectromechanical Systems", vol. 6, pp. 99–106.

147 P.S. Theocaris, G.E. Stavroulakis, P.D. Panagiotopoulos, (1997), *Negative Poisson's ratios in composites with star-shaped inclusions: a numerical homogenization approach*, "Archive of Applied Mechanics", vol. 67, pp. 274–286.

148 Z.P. Wang, L.H. Poh, J. Dirrenberger, Y. Zhu, S. Forest, (2017), *Isogeometric shape optimization of smoothed petal auxetic structures via computational periodic homogenization*, "Computer Methods in Applied Mechanics and Engineering", vol. 323, pp. 250–271.

149 X.T. Wang, B. Wang, X.W. Li, L. Ma, (2017), *Mechanical properties of 3D re-entrant auxetic cellular structures*, "International Journal of Mechanical Sciences", vol. 131, pp. 396–407.

rigid or semi-rigid units,[150, 151, 152, 153, 154, 155] chiral structures,[156, 157] filamentous / nodular structures,[158, 159] spiral auxetic yarn.[160]

'Re-entrant' honeycomb structures represent one of the earliest developed models of structures proving the Negative Poisson's Ratio. The adjective 're-entrant' means that the shape has an angle in its structure greater than 180° pointing inwards (Fig. 2.12.).

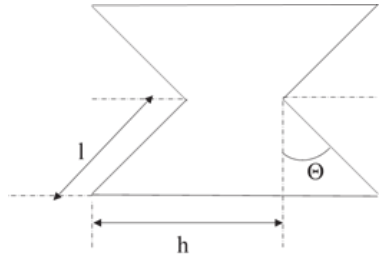

Figure 2.12. The basic hexagonal cell of the re-entrant honeycomb structure
Source: own elaboration according to W. Miller, P.B. Hook, C.W. Smith, X. Wang, K.E. Evans, (2009), *The manufacture and characterisation of a novel, low modulus, negative Poisson's ratio composite*, "Composites Science and Technology", vol. 69, pp. 651–655.

150 J.N. Grima, K.E. Evans, (2000), *Auxetic behavior from rotating squares*, "Journal of Materials Science Letters", vol. 19, pp. 1563–1565.

151 J.N. Grima, P.S. Farrugia, R. Gatt, D. Attard, (2008), *On the auxetic properties of rotating rhombi and parallelograms: a preliminary investigation*, "Physica Status Solidi B.", vol. 245, pp. 521–529.

152 J.N. Grima, R. Gatt, A. Alderson, K.E. Evans, (2005), *On the auxetic properties of rotating rectangles with different connectivity*, "Journal of the Physical Society of Japan", vol. 74, pp. 2866–2867.

153 J.N. Grima, E. Chetcuti, E. Manicaro, D. Attard, M. Camilleri, R. Gatt, K.E. Evans, (2011), *On the auxetic properties of generic rotating rigid triangles*, Proceedings of the Royal Society of London A, vol. 468, pp. 810–830.

154 S. Shan, S.H. Kang, Z. Zhao, L. Fang, K. Bertoldi, (2015), *Design of planar isotropic negative Poisson's ratio structures*, "Extreme Mechanics Letters", vol. 4, pp. 96–102.

155 J. Kim, D. Shin, D.S. Yoo, K. Ki, (2017), *Regularly configured structures with polygonal prisms for three-dimensional auxetic behavior*, Proceedings of the Royal Society of London A, vol. 473, 20160926.

156 D. Prall, R.S. Lakes, (1997), *Properties of a chiral…*

157 J.N. Grima, R. Gatt, P.S. Farrugia, (2008), *On the properties of auxetic meta-tetrachiral structures*, "Physica Status Solidi B.", vol. 245, pp. 511–520.

158 K.E. Evans, B.D. Caddock, (1989), *Microporous materials with negative Poisson's ratios II, Mechanisms and interpretation*, "Journal of Physics D: Applied Physics", vol. 2, pp. 1877–1883.

159 C. He, P. Liu, A.C. Griffin, (1998), *Toward negative Poisson ratio polymers through molecular design*, "Macromolecules", vol. 31, pp. 3145–3147.

160 W. Miller, P.B. Hook, C.W. Smith, X. Wang, K.E. Evans, (2009), *The manufacture and characterisation of a novel, low modulus, negative Poisson's ratio composite*, "Composites Science and Technology", vol. 69, pp. 651–655.

A graphical elaboration of two-dimensional re-entrant auxetic structures: the honeycomb triangular structure and the star-shaped structure can be found in the Handbook of Mechanics of Materials.[161] Three-dimensional re-entrant structures are well-illustrated by the authors of the publication "Mechanical Properties of 3D Re-entrant Auxetic Cellular Structures".[162]

Structures consisting of the so-called rigid or semi-rigid rotating units.

Structures consisting of the so-called rigid or semi-rigid rotating units account for still another model of structures that may have auxetic properties. Rotating mechanism structures consist of rigid units connected by hinges. The rigid units are arranged according to a consistent principle, and their initial positions are slightly inclined in a clockwise or anti-clockwise direction, which is opposite to the direction of tilt of the neighbouring units.

Chiral structures

The so-called chiral structures represent another model of an auxetic structure that is for the first time presented by Prall and Lakes in the context of the Negative Poisson's Ratio.[163, 164] The word chiral denotes the non-overlap of an object with its mirror image. A single auxetic structure consists of central nodes that are circles, rectangles or other geometric figures, and connectors (ligaments). A chiral structure is formed by connecting multiple single cells. The auxetic effect is achieved by wrapping and unwrapping the linkers around the nodes in response to a given force.

Fibre/nodule structures

The effect of the Negative Poisson's Ratio is achieved by an internal structure consisting of coarsening/thicknesses connected by fibre. Under load, the knobs rotate around the fibres, giving rise to an auxetic property.

161 H. Cho, D. Seo, D.N. Kim, (2019), *Mechanics of Auxetic Materials*, [in:] CH. Hsueh et al. (eds), *Handbook of Mechanics of Materials,* Springer, Singapore.

162 X.T. Wang, B. Wang, X.W. Li, L. Ma, (2017), *Mechanical properties…*

163 D. Prall, R.S. Lakes, (1997), *Properties of a chiral…*

164 C. He, P. Liu, A.C. Griffin, (1998), *Toward negative…*

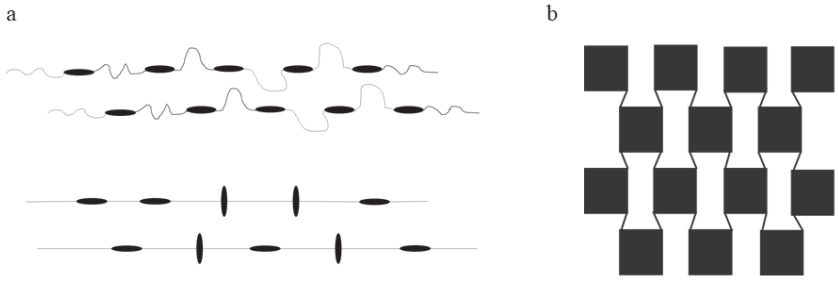

Figure 2.13. Typical shape of fibril-nodule structures: (a) single fibril-type structural model for a liquid crystalline polymer (bundle type), (b) multifibril structures with rectangular nodules/thickenings (lattice type)
Source: I. Masłowska-Lipowicz, Ł. Wyrębska, B. Szałek, P. Olszewski, R. Gajewski, (2020), *Materiały auksetyczne – struktury, potencjalne zastosowanie*, „Technologia i Jakość Wyrobów", vol. 65, pp. 116–128.

Helical Auxetic Yarn

Spiral auxetic yarn is a unique auxetic material that consists of two types of thread.[165, 166] The core thread is a thick but flexible thread that has a straight shape in its unstressed state. The core thread is wrapped with a thin and 'stiff' thread that is the second component of the auxetic yarn. The effective diameter of the yarn is the sum of the diameter of the core thread and twice the diameter of the spiral thread wrapped around it. When a tensile load is applied to the spiral yarn, a radical change occurs due to the difference in stiffness values between the two threads – the spiral-wound stiffer (wrapping) thread straightens in the direction of the tensile load. As a result, the core thread is now spirally wound around the stiffer thread. In such a state, the effective diameter of the deformed shape is defined as the diameter of the wrapping thread plus twice the diameter of the core thread (it is larger than the diameter of a single yarn fibre in the initial state, increasing under tensile load). As a result, the entire fabric composed of helical auxetic yarn proves the NPR and stretches in the direction perpendicular to the applied load.

Potential applications

Auxetic materials and the models describing their properties are subject to intensive research, not only in terms of basic research, but also in terms of potential applications. The auxetic response of materials derives from the deformation mechanism of specific geometries and internal structures in result of uniaxial loads. As compared to conventional materials with the Positive Poisson's Ratio, auxetic materials are expected to have several interesting features in terms of their

165 W. Miller, P.B. Hook, C.W. Smith, X. Wang, K.E. Evans, (2009), *The manufacture and…*
166 Z. Ge, H. Hu, S. Liu, (2016), *A novel plied yarn structure with negative Poisson's ratio*, "The Journal of the Textile Institute", vol. 107, no. 5, pp. 578–588.

geometrical and mechanical properties, including synclastic bending curvature,[167, 168] variable permeability,[169] high shear stiffness,[170, 171] enhanced dent resistance,[172, 173, 174] high fracture toughness[175, 176, 177, 178] and sound damping, and absorption.[179, 180, 181, 182] Those remarkable properties offer a wide range of applications for auxetic materials, inter alia, in biomedical materials,[183] cushioning materials,[184] energy harvesting

167 R.S. Lakes, (1987), *Foam structures with a negative Poisson's ratio*, "Science", vol. 235, pp. 1038–1041.

168 K.E. Evans, A. Alderson, (2000), *Auxetic materials: functional materials and structures from lateral thinking,* "Advanced Materials", vol. 12, pp. 617–28.

169 Z. Wang, H. Hu, (2014), *Auxetic materials and their potential applications in textiles*, "Textile Research Journal", vol. 84, pp. 1600–1611.

170 K.E. Evans, A. Alderson, (2000), *Auxetic materials…*

171 R.S. Underhill, (2014), *Defense applications of Auxetic materials*, "Advanced Materials", vol. 1, pp. 7–13.

172 K.E. Evans, A. Alderson, (2000), *Auxetic materials…*

173 K.L. Alderson, A.P. Pickles, P.J. Neale, K.E. Evans, (1994), *Auxetic polyethylene: the effect of a negative Poisson's ratio on hardness*, "Acta Metallurgica et Materialia", vol. 42, pp. 2261–2266.

174 Q. Liu, (2006), *Literature review: materials with negative Poisson's ratios and potential applications to aerospace and defence*, Defence Science and Technology Organisation, Victoria.

175 R.S. Lakes, (1987), *Foam structures…*, pp. 1038–1041.

176 J.B. Choi, R.S. Lakes, (1996), *Fracture toughness of re-entrant foam materials with a negative Poisson's ratio: experiment and analysis*, "International Journal of Fracture", vol. 80, pp. 73–83.

177 J.P. Donoghue, K.L. Alderson, K.E. Evans, (2009), *The fracture toughness of composite laminates with a negative Poisson's ratio*, "Physica Status Solidi B.", vol. 246, pp. 2011–2017.

178 S.K. Maiti, M.F. Ashby, L.J. Gibson, (1984), *Fracture toughness of brittle cellular solids*, "Scripta Metallurgica", vol. 18, pp. 213–217.

179 I. Chekkal, M. Bianchi, C. Remillat, F.X. Becot, L. Jaouen, F. Scarpa, (2010), *Vibro-acoustic properties of auxetic open cell foam: model and experimental results*, "Acta Acustica United Acustica", vol. 96, pp. 266–274.

180 B. Howell, P. Prendergast, L. Hansen, (1994), *Examination of acoustic behavior of negative Poisson's ratio materials*, "Applied Acoustics", vol. 43, pp. 141–148.

181 K.L. Alderson, R.S. Webber, U.F. Mohammed, E. Murphy, K.E. Evans, (1997), *An experimental study of ultrasonic attenuation in microporous polyethylene*, "Applied Acoustics", vol. 50, pp. 23–33.

182 F. Scarpa, L.G. Ciffo, J.R. Yates, (2003), *Dynamic properties of high structural integrity auxetic open cell foam*, "Smart Materials and Structures", vol. 13, p. 49.

183 S.K. Bhullar, N.L. Lala, S. Ramkrishna, (2015), *Smart biomaterials – a review*, "Reviews on Advanced Materials Science", vol. 40, pp. 303–314.

184 N. Novak, M. Vesenjak, Z. Ren, (2016), *Auxetic cellular materials – a review*. "Strojniški Vestnik – Journal of Mechanical Engineering", vol. 62, pp. 485–493.

devices,[185] sports equipment,[186] filters,[187] robotics,[188] textiles[189, 190] or materials used in the aerospace industry[191] and construction.[192] Medical applications include auxetic bandage that effectively compresses a wound as well as the so-called stents that cause the cross-section through which blood flows to be increased, creating a kind of artificial blood vessel that resists dangerous constriction of the vessel cross-section.[193]

Auxetic textiles

Auxetic textile materials (fibre, yarn, fabric, textile-reinforced composites) have been of interest to many researchers in recent years. Although most of the literature refers to auxetic textile that has better properties than conventional materials, very few types of auxetic materials have been manufactured on a scale larger than the laboratory scale. The major limitations of manufacturing auxetic textiles include: low structural stability, low elastic return, greater thickness and difficulty in manufacturing due to their complex geometric structures. Undoubtedly, auxetic textile shows a great potential to be classified as smart textile to be used, for example, in the manufacture of clothing, but this is a matter of research that is still ongoing.

In a US patent,[194] a multilayer sole was developed, in which one layer has auxetic properties, during an activity (running, jumping, etc.), causing increased lateral or longitudinal stress, better grip (by increasing surface area) as well as cushioning.

185 G. Imbalzano, P. Tran, T.D. Ngo, P.V. Lee, (2017), *Three-dimensional modelling of auxetic sandwich panels for localised impact resistance*, "Journal of Sandwich Structures & Materials", vol. 19, no. 3, pp. 291–316.

186 K.L. Alderson, A.P. Pickles, P.J. Neale, K.E. Evans, (1994), *Auxetic polyethylene…*

187 A. Alderson, J. Rasburn, S. Ameer-Beg, P.G. Mullarkey, W. Perrie, K.E. Evans, (2000), *An auxetic filter: a tuneable filter displaying enhanced size selectivity or defouling properties*, "Industrial & Engineering Chemistry Research", vol. 39, no. 3, pp. 654–665.

188 A.G. Mark, S. Palagi, T. Qiu, P. Fischer, (2016), *Auxetic metamaterial simplifies soft robot design*, "2016 IEEE International Conference on Robotics and Automation (ICRA)", pp. 4951–4956.

189 K.E. Evans, A. Alderson, (2000), *Auxetic materials…*

190 M. Konaković, K. Crane, B. Deng, S. Bouaziz, D. Piker, M. Pauly, (2016), *Beyond developable: computational design and fabrication with auxetic materials*, "ACM Transactions on Graphics (TOG)", vol. 35, pp. 79–89.

191 R.S. Underhill, (2014), *Defense applications…*

192 D. Park, J. Lee, A. Romo, (2015), *Poisson's Ratio Material Distributions*, [in:] Y. Ikeda, C.M. Herr, D. Holzer, S. Kaijima, M.J. Kim, A. Schnabel (eds), *In Emerging Experience in Past, Present and Future of Digital Architecture, Proceedings of the 20th International Conference of the Association for Computer-Aided Architectural Design Research in Asia CAADRIA 2015*, Hong Kong, pp. 725–744.

193 S.K. Bhullar, N.L. Lala, S. Ramkrishna, (2015), *Smart biomaterials…*

194 T.M. Cross, K.W. Hoffer, D.P. Jones, P.B. Kirschner, E. Langvin, J.C. Meschter, US-9402439-B2, *Auxetic structures and footwear with soles having auxetic structures*.

The effectiveness of the auxetic footbed in reducing forefoot pressure during the use of high-heeled shoes has been confirmed. The use of auxetic foam decreases forefoot sole pressure whereas a commercial product, a material traditionally used for sole padding, increases pressure in the area of the second-fourth metatarsophalangeal joint.[195]

The right way of deforming under tension makes auxetics a protective material that may be used in items that protect people from injury or the effects of any impact. Protective helmets, footwear, bulletproof vests or knee and shin guards are made from them.

Clothing or shoes made from auxetics adjust very easily to the shape of the human body improving ergonomics and comfort and, in the case of children's textile, can eliminate the problem of short use of garments due to the rapid growth of children (growing clothes).[196, 197]

The wide use of auxetic materials results from their properties, e.g. synclastic bending curvature, variable permeability, high shear stiffness, increased dent resistance, high fracture toughness and sound attenuation and absorption. Potential areas of application for auxetics include biomedical materials, cushioning, energy harvesting devices, sports equipment, filters, robotics, textiles or materials used in the aerospace and construction industries.

Auxetic materials have enormous potential but their production for widespread use is still limited. The issue requires further research into both the properties and applicability of auxetic materials.

195 L.A. Stojmanovski Mercieca, C. Formosa, J.N. Grima, N. Chockalingam, R. Gatt, A. Gatt, (2017), *On the Use of Auxetics in Footwear: Investigating the Effect of Padding and Padding Material on Forefoot Pressure in High Heels*, "Physica Status Solidi B", vol. 254, no. 12, 1700528.

196 H. Cho, D. Seo, D.N. Kim, (2019), *Mechanics of Auxetic…*

197 R.S. Underhill, (2014), *Defense applications…*